g (0.2 mol) of phosgene in 100 ml of dry chlorobenzene. After completion of addition the reaction mixture was slowly heated to 50°, and after stirring for 90 min the solvent was removed by distillation. Vacuum distillation of the residue gave 13 g (91%) of a slightly impure *N*-phenyl-*N*-4-isocyanatobenzylcarbamoyl chloride (**9**), containing small amounts of phenyl (**4**) and 4-chloromethylphenyl isocyanate (**11**), as indicated by glc. Repeated fractional distillation produced pure **9**: bp 166° (0.25 mm); ir ($CHCl_3$) 2247 cm^{-1} (N=C=O), 1739 cm^{-1} (C=O); nmr ($CDCl_3$) δ 4.85 (s, 2, CH_2). *Anal.* Calcd for $C_{15}H_{11}N_2O_2Cl$: C, 62.84; H, 3.87; N, 9.77. Found: C, 62.96; H, 3.97; N, 10.05.

In a larger scale experiment (0.15 mol) phenyl isocyanate (**4**), [bp 39° (0.005 mm)] and 4-chloromethylphenyl isocyanate (**10**) [bp 68° (0.005 mm), mp 31–33° (lit.[9] mp 34°)] were isolated by fractional distillation.

Reaction with Methanol. A solution of 2.86 g (0.01 mol) of **9** in 10 ml of methanol was allowed to stand at room temperature overnight. Concentration of this solution gave 2.91 g (92%) of the methyl carbamate **11**, mp 108–109° after recrystallization from methanol. *Anal.* Calcd for $C_{16}H_{15}N_2O_3Cl$: C, 60.28; H, 4.74; N, 8.79. Found: C, 60.10; H, 4.95; N, 8.77.

Reaction with Hydrogen Chloride. A slow stream of dry hydrogen chloride was added to a refluxing solution of 1.5 g of **9** in 15 ml of dry chlorobenzene. After refluxing for 4 hr, complete conversion to **4** and **10** was observed as indicated by monitoring of the reaction mixture by nmr spectroscopy and glc.

Acknowledgment. We are indebted to F. P. Recchia and E. Goerland, who conducted part of the experimental investigation.

Registry No.—**1**, 622-14-0; **2**, 91-78-1; **3**, 24007-66-7; **4**, 103-71-9; **5**, 52123-54-3; **6**, 4285-42-1; **7**, 52123-55-4; **9**, 52123-56-5; **11**, 52123-57-6; phosgene, 75-44-5; nitrobenzylideneaniline, 785-80-8; methanol, 67-56-1; hydrogen chloride, 7647-01-0.

References and Notes

(1) P. Cohn, *Z. Angew. Chem.*, **14**, 313 (1901).
(2) M. Wakae and K. Konishi, *Osaka Furitsu Kogyo-Shoreikan Hokoku*, **29**, 47 (1963); *Chem. Abstr.*, **59**, 6280 (1963).
(3) O. Fischer, *Ber.*, **14**, 2525 (1881).
(4) C. Paal and O. Sprenger, *Ber.*, **30**, 69 (1897).
(5) H. Babad and A. G. Zeiler, *Chem. Rev.*, **73**, 75 (1973).
(6) J. N. Tilley and A. A. R. Sayigh, *J. Org. Chem.*, **28**, 2076 (1963).
(7) Melting and boiling points are uncorrected. Analyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Ir spectra were determined using a Beckman IR-8 spectrophotometer. Nmr spectra were obtained from samples in $CDCl_3$ solutions with a Varian T-60 instrument using tetramethylsilane as the internal standard. Gas chromatography was carried out on a Model 810 F & M gas chromatograph; 5% silicon grease columns were used. Gel permeation chromatography was conducted on a Waters 200 chromatograph.
(8) The indicated per cent values are by area ratio.
(9) British Patent 752,931 (1956); Farbenfabriken Bayer A.-G.; *Chem. Abstr.*, **51**, 7420 (1957).

Carbon-13 Magnetic Resonance Spectral Study of Some Phosphorinanes and Their 1-Sulfides[1]

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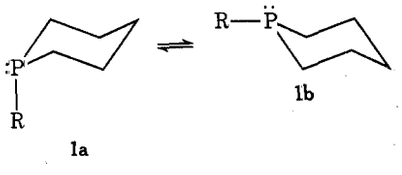
The ^{13}C nmr spectra of a group of five 1-substituted phosphorinanes (**1**) and of their corresponding sulfides (**4**) were obtained. Chemical shift trends within each group can be interpreted in terms of the familiar α,β,γ effects. The known axial predominance in **1** of *P*-methyl, -ethyl, and -phenyl is manifested in their ^{13}C spectra by slightly higher field $C_{3,5}$ signals than seen for the *tert*-butyl and isopropyl compounds, and also by the small value for the sterically sensitive $^2J_{PC_{3,5}}$ in the former (3.0–3.5 Hz) relative to the latter compounds (6–7 Hz). In the sulfides, all compounds appear to have a predominance of the conformer with equatorial carbon substituent, as judged from shift effects at $C_{2,6}$ and $C_{3,5}$. Of value in reaching this conclusion was a comparison of the spectra of the conformationally biased 1,4-disubstituted 4-phosphorinanols with their sulfides. The greater shielding exerted at $C_{3,5}$ by axial sulfur rather than by axial methyl was especially useful in this study. The ^{31}P nmr signal was the more upfield for that isomer where the steric compression was the greatest.

Carbon-13 nmr spectroscopy has been employed with much success in the determination of structural and stereochemical features of several types of six-membered heterocyclic compounds.[2d] Little is known, however, about the ^{13}C properties of the ring where phosphorus is the heteroatom; only 4-hydroxy derivatives of this system have been studied so far.[3,4] This phosphorinane system is of special interest because of the remarkably small value for $\Delta H°$ in the equilibrium of **1a** and **1b** (−0.68 kcal/mol for R = CH_3).[5] Indeed, entropy effects cause the equilibrium position at 27° to rest on the side of the axial conformer when R is methyl (K = 0.56),[5] ethyl (K = 0.65),[6] or phenyl (K = 0.72).[6] We have now obtained the ^{13}C nmr spectra of these and other 1-substituted phosphorinanes and have established relations between chemical shifts and structural and conformational properties of this system.



1a **1b**

Carbon spectra of phosphorus compounds contain more information than just chemical shift values; the ^{31}P atom couples with carbon to produce doublets of easily measured magnitude through two and sometimes three bonds. The size of two-bond coupling for trivalent phosphorus is subject to steric control[3,7,8] and consequently is of value in conformational analysis.

We have included in our study a consideration of the consequences of adding a fourth group to phosphorus. We have used the sulfides of the phosphorinanes for this purpose, since they are easily prepared, nonhygroscopic crystalline solids. While a proton nmr conformational study of the sulfide of phosphorinane itself (**1**, R = H) has been reported,[9] no attention has been given previously to the stereochemical consequences of placing both sulfur and an alkyl group on phosphorus.

Phosphorinanes. Carbon-13 nmr data for five 1-substituted phosphorinanes are recorded in Table I. Assignments were made as follows. (1) Relative to a carbon substituent, the phosphino group shields the attached carbons, presumably because of weak inductive electron displacement to carbon. This causes the carbon of the PCH_3 group (mostly axial[5]) to absorb about 5 ppm upfield from CH_3 when axial

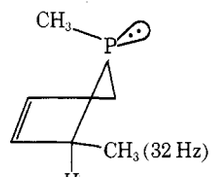
Table I
^{13}C Nmr Spectra of Phosphorinanes[a]

Registry no.	1, R =	δ $C_{2,6}$	δ $C_{3,5}$	δ C_4	δ P–C	δ P–C–C
39763-50-3	CH_3	165.8 (13)	169.1 (3)	164.2 (2)	181.6 (19)	
52032-39-0	CH_3CH_2	167.6 (14)	168.8 (4)	164.1 (3)	172.4 (14)	182.8 (16)
52032-40-3	$(CH_3)_2CH$	168.4 (12)	168.6 (6)	164.2 (2)	166.1 (12)	173.5 (17)
52032-41-4	$(CH_3)_3C$	171.1 (18)	167.5 (7)	164.1 (3)	169.1 (28)	165.8 (14)
3302-83-8	C_6H_5	167.9 (14)	169.1 (4)	164.6 (2)		

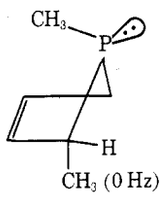
[a] See ref 25 for experimental details. Chemical shifts were determined on neat samples from internal TMS and are calculated from CS_2 as standard. ^{31}P–^{13}C coupling constants (in hertz) are given in parentheses.

on the cyclohexane ring.[10] Its signal is easily recognized. (2) The coupling of trivalent phosphorus with adjacent carbon is generally about 12–15 Hz, also assisting in the recognition of the exocyclic carbon, as well as of $C_{2,6}$ of the ring. (3) C_4 is least affected by the presence of phosphorus; of the ring carbons it gives the most downfield peak, which is of half the intensity of the ring carbon signals. (4) The chemical shift and phosphorus coupling of $C_{3,5}$ are influenced by conformational effects to be discussed subsequently. Generally, the coupling at $C_{3,5}$ was much smaller than at $C_{2,6}$, and this was an aid in the assignments.

Within the family, certain trends are clearly discernible for the ring carbons. (1) As methyls replace hydrogen on the exocyclic carbon attached to phosphorus, the chemical shift of $C_{2,6}$ progresses to higher field. This is explainable on the basis of the well-known[2b] γ effect, in this case operating through P in the fragment C_γ–C_β–P_α–$C_{2,6}$ and increasing with the number of γ carbons. Coupling of $C_{2,6}$ to ^{31}P is consistently 11.5–13.5 Hz except for the *tert*-butyl case, where it rises to 17.5 Hz. Similarly, the exocyclic C–P coupling in the *tert*-butyl derivative is considerably larger than in the other compounds. This effect has been observed elsewhere for acyclic *tert*-butyl phosphines[11] and is believed to be the result of increased bond angles about the phosphorus atom in this more crowded system. (2) $C_{3,5}$ are susceptible to a γ effect from the exocyclic P substituent ($C_\gamma P_\beta C_\alpha C_{3,5}$). If the substituent is axially oriented, the effect will be maximal, since $C_{3,5}$ are then gauche related to this substituent. As the size of the P substituent increases, the conformational equilibrium should shift so that the equatorial conformer concentration is increased. Low-temperature ^{31}P nmr measurements have indicated this to be the case.[5,6] The data in Table I show that δ $C_{3,5}$ for the various phosphorinanes does vary in accord with the conformational effect; δ $C_{3,5}$ moves to lower field as the substituent size increases. However, relative differences in the γ effect of various P substituents could also influence δ $C_{3,5}$. The magnitude of the two-bond phosphorus coupling to $C_{3,5}$ is more specifically related to the position of conformational equilibrium. In freely rotating acyclic phosphines $^2J_{PC}$ is about 12–15 Hz,[11,12] but in cyclic phosphines the value can vary from 0 to 32 Hz.[7,8] The large values seem to occur in systems where the dihedral angle relating the phosphorus lone-pair orbital to the coupled carbon is small,[7] as for the 2-methyl of *cis*-1,2-dimethyl-3-phospholene[8] (shown as conformation **2a**). Negligible coupling

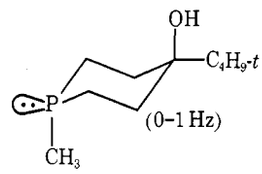


2a

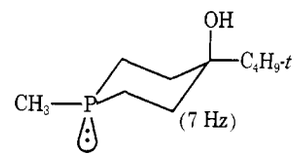


2b

occurs in the trans isomer **2b**, and for $C_{3,5}$ of the ring in *trans*-1-methyl-4-*tert*-butyl-4-phosphorinanol[3] (**3a**); in



3a



3b

both the pertinent dihedral angle is large. Coupling is small but significant (7 Hz) for the cis isomer of the 4-phosphorinanol (**3b**) where $C_{3,5}$ and the lone pair are in closer proximity than the trans isomer.[3] It is obvious that $^2J_{PC}$ is very much dependent on steric relations, and with definite dihedral angle values a useful stereochemical tool would be at hand;[13] for the present the relation must remain qualitative. Nevertheless, the limits appear defined for the phosphorinane ring by **3a** and **3b** with axial and equatorial substituents. The $^2J_{PC}$ values for $C_{3,5}$ of the 1-substituted phosphorinanes of Table I may then be compared to these limits. The largest value (7 Hz) is seen for the 1-*tert*-butyl compound; since this value is the same as for compound **3b**, the implication is clear that the *tert*-butyl group on phosphorus is predominantly equatorial. This is supported by the low-temperature ^{31}P studies.[6] The isopropyl group is also suggested from its value of 6 Hz to be largely equatorial. The smaller values (about 3 Hz) for the remaining compounds are in keeping with a conformational equilibrium mixture having a considerable concentration of the axial conformer, as found also from the ^{31}P studies.[5,6] (3) The chemical shift of C_4 is remarkably constant for the series (164.1–164.6), and is consistently downfield from the range for comparable alkylcyclohexanes (166.2–166.7 ppm).[2a] This is quite in keeping with the trend established among noncyclic phosphines; in the structure $XCH_2CH_2CH_2CH_3$, the γ carbon is farther downfield by about 2 ppm when X is a tertiary phosphine group than when X is methyl.[12] The reverse trend is seen for nitrogen; in both piperidines[2e] and noncyclic amines,[14] the γ carbon is upfield of that in the cyclohexanes and alkanes, respectively.

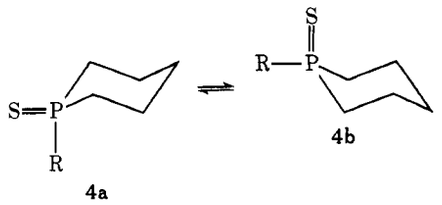
Phosphorinane Sulfides. Spectral data for the sulfides (**4**) of the five phosphorinanes are given in Table II. Assignments of carbons attached directly to phosphorus were easily made because of the large coupling constants, typically 45–50 Hz. Relative to the phosphines, the sulfides have chemical shifts for attached carbons that are several parts per million downfield. This effect has also been observed for acyclic sulfides.[2c] In the ring, coupling was substantial (5–8 Hz) at both $C_{3,5}$ and C_4; the latter signal was readily recognized from its intensity relation. Unlike for the phosphine, $^1J_{PC}$ for 1-*tert*-butylphosphorinane sulfide did not differ from the range seen for the other members of the series.

Table II
^{13}C Nmr Spectra of Phosphorinane Sulfides[a]

Registry no.	4, R =	δ $C_{2,6}$	δ $C_{3,5}$	δ C_4	δ P–C	δ P–C–C
1661-16-1	CH_3	159.8 (49)	170.1 (6)	166.3 (8)	174.0 (53)	
52032-42-5	CH_3CH_2	162.2 (48)	170.6 (8)	166.1 (6)	168.5 (50)	186.7 (5)
52032-43-6	$(CH_3)_2CH$	163.7 (48)	171.3 (8)	166.0 (7)	164.3 (50)	177.4 (0)
52032-44-7	$(CH_3)_3C$	167.9 (47)	171.7 (7)	165.6 (7)	159.8 (50)	168.2 (0)
4963-94-4	C_6H_5	160.6 (50)	170.7 (6)	165.9 (8)		

[a] See ref 25 for experimental details. Chemical shifts were determined from internal TMS and are calculated from CS_2 = 0; ^{31}P–^{13}C coupling constants (hertz) are given in parentheses. Samples were run in chloroform.

Several trends are apparent in the family. (1) At $C_{2,6}$ a steady upfield progression of the ^{13}C shift occurs as the protons of the PCH_3 group are replaced by methyl. This γ effect is the same as observed in the phosphine family. (2) At $C_{3,5}$ the chemical shift moves upfield with an increase in the size of the *P*-alkyl substituent and hence with its degree of equatorial character. This is the reverse of the trend seen in the phosphines, but is easily accounted for from an observation made in previous work[4] and discussed further in the next section: in the 4-phosphorinanol sulfides, greater shielding at $C_{3,5}$ is found for axial sulfur than for axial methyl. Although proton nmr studies[9] have suggested that the sulfur prefers the equatorial position when a proton is on phosphorus in **4**, the conformational equilibrium for the phosphorinane sulfides may be presumed to shift to the right when the proton is replaced by an alkyl substituent, the shift increasing with the size of the alkyl group. There



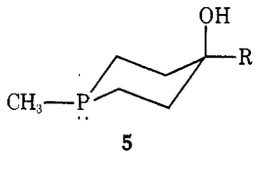
4a **4b**

is consequently increased shielding at $C_{3,5}$ since the contribution of the conformer with axial sulfur is greater. The chemical shift of $C_{3,5}$ is therefore intimately associated with the position of the conformational equilibrium. It is very likely that the *P-tert*-butyl group is largely equatorial, as usual, and that the *P*-methyl group has considerably more axial character. (3) C_4 shows the same chemical shift constancy within the series as observed for the phosphines. The range covered (165.6–166.3 ppm) is slightly to higher field than that of the phosphines (164.1–164.6 ppm), and is similar to the range for some alkylcyclohexanes (166.2–166.7 ppm).[2a] A steady progression of δ C_4 to lower field does occur for the sulfides as the size of the alkyl group increases, but the effect is small.

The position of the conformational equilibrium in the phosphorinane sulfides should be controlled by the relative magnitude of the nonbonded interactions of alkyl *vs.* sulfur with the axial protons at $C_{3,5}$. It might be anticipated that these interactions would be more severe with the alkyl group, and molecular parameters as determined by X-ray analysis support this position.[4] The interactions would of course increase with the size of the alkyl group. Two pieces of evidence suggest that even in 1-methylphosphorinane sulfide the conformer with equatorial methyl is dominant in the equilibrium. (1) As will be discussed further in the next section, the placement of sulfur on the axial site in a 1,4-dimethyl-4-phosphorinanol (conformationally biased) causes an *upfield* shift (2.5 ppm) at $C_{3,5}$, but placement on the equatorial site causes a *downfield* shift (1.8 ppm). These changes can then serve as a basis for a similar consideration of the sulfurization of 1-methylphosphorinane. Here it must be assumed that a new equilibrium position will be attained after the addition of sulfur, to reflect the relative preferences of methyl and sulfur. The fact that *shielding* at $C_{3,5}$ (by 1.0 ppm) accompanies the sulfurization strongly suggests that the sulfur is largely in the axial position, for if methyl remained in the axial position that it prefers in the phosphorinane, then a downfield shift at $C_{3,5}$ would have taken place and deshielding, rather than the observed shielding, would occur at $C_{3,5}$. (2) At $C_{2,6}$, there is deshielding by 6.0 ppm when 1-methylphosphorinane is sulfurized. When the phosphorinanol isomer with axial methyl is sulfurized, the deshielding is 8.7 ppm, while only 5.2 ppm is realized when the equatorial form is sulfurized. It is therefore again implied that sulfurization of the axial form of 1-methylphosphorinane is followed by a shift in the position of equilibrium to the side with equatorial methyl. In future work, we expect to determine the conformation adopted by 1-methylphosphorinane sulfide in the solid state by X-ray analysis.

An important effect also occurs at an exocyclic carbon β to phosphorus on conversion of a phosphine to its sulfide. In 1-ethylphosphorinane, the methyl of the substituent is shifted 3.9 ppm upfield on addition of sulfur. If the sulfur atom is considered as an added β substituent to the methyl, the upfield shift becomes understandable. The same effect is seen for the methyls of the isopropyl (3.9 ppm) and *tert*-butyl (2.4 ppm) substituents.

The 4-Phosphorinanol Series. Some of the effects observed in the phosphorinanes on sulfurization are clearly evident in 4-hydroxy derivatives as well, for which spectral data have been presented previously.[3,4] This system has the desirable feature that, when a 4-alkyl (or phenyl) substituent is also present, the resulting cis–trans isomers each have conformational equilibria strongly biased towards the conformer with equatorial orientation of this substituent (**5** and **6**, respectively). On sulfurization, compounds with



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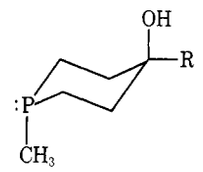


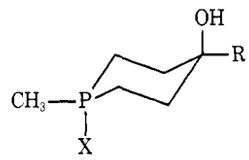
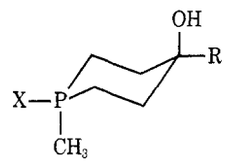
6

known orientation of the P substituents result, since this reaction is stereospecific (retention[15]).

Considering first the placement of axial sulfur on the ring (**5** → **7**), deshielding by the β effect is noticed at $C_{2,6}$, while γ shielding is noted at $C_{3,5}$ (Table IIIA). At C_4, the shielding effect on sulfurization discussed previously for the phosphorinanes is noticeable.

Placement of equatorial sulfur (Table IIIB) causes great-

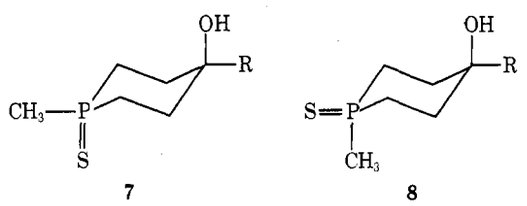
Table III
Changes[a] of ^{13}C Shifts on Converting 4-Phosphorinanols to Their Sulfides[b]

R	Δδ $C_{2,6}$	Δδ $C_{3,5}$	Δδ C_4
A. 			5, X = lone pair 7, X = S
CH_3	−5.2	+2.5	+1.1
t-C_4H_9	−3.1	+3.9	+0.5
C_6H_5	−3.1	+3.7	+0.8
B. 			6, X = lone pair 8, X = S
CH_3	−8.7	−1.8	+1.2
t-C_4H_9	−10.0	−4.2	+1.3
C_6H_5	−9.7	−3.9	+2.9

[a] Negative sign means deshielding accompanies the conversion to the sulfide; positive sign means shielding occurs. [b] Spectral data for the 4-phosphorinanols are given in ref 3, and for the sulfides in ref 4.

er deshielding at $C_{2,6}$ than accompanies axial placement, and deshielding occurs at $C_{3,5}$ as well. The effect at $C_{3,5}$ possibly due to the bond angle changes at phosphorus; these angles are increased in the sulfide owing to the greater s character, and this might tend to lessen the steric crowding of axial methyl with the axial 3,5 protons, thus causing a downfield shift relative to the phosphine. Geometric deformations are known to modify the size of the γ effect for gauche interactions of carbon atoms in carbocyclic systems.[16]

That the $C_{3,5}$ signals for the axial sulfur series (7) are more upfield than those for the axial methyl series (6) is



7 8

a, R = CH_3
b, R = t-C_4H_9
c, R = C_6H_5

the point mentioned earlier in this paper that led to the suggestion[4] of greater γ shielding by sulfur than methyl. This rather surprising result should not be taken to mean that the "size" of sulfur is greater than that of methyl; data from cyclohexanes are available to show that the magnitude of the γ-shielding effect of heteroatom substituents depends on other factors than size of the substituent alone. Thus, axial OH and axial F both exert a greater shielding effect on $C_{3,5}$ than does axial CH_3.[17] Another manifestation of this effect may be seen on N-oxidation (presumably axial) of *N*-methylpiperidine; $C_{3,5}$ are shielded by 5.1 ppm,[2e] a strikingly large amount for an atom the size of oxygen.[18] Also, an axial oxygen on sulfur of a 1,3,2-dioxathiane causes shielding at $C_{4,6}$ of 9 ppm relative to the equatorial isomer.[20]

Finally, we can derive evidence from ^{31}P spectra that the steric compression is greater for the compound with the axial methyl substituent. We have pointed out elsewhere[21] that in acyclic phosphorus compounds, both tri- and tetrasubstituted, the ^{31}P atom is deshielded by carbons located β to it and shielded by γ carbons, just as is true for ^{13}C shifts. It follows that in cyclic compounds steric effects influencing carbon shifts should also influence phosphorus shifts. Therefore, steric compression should shield phosphorus in the phosphorinane ring as it does carbon in the ring of crowded cyclohexanes.[2b] In Table V are given ^{31}P nmr data for the isomeric 4-phosphorinanol sulfides, and in every case the most upfield signal is associated with the isomer with axial methyl, as expected. This relation appears to hold in other series as well, and constitutes a useful tool for isomer assignment. For example, in the 1,3,2-dioxaphosphorinane oxides[22] and sulfides,[23] an axial $-OCH_3$ or $-N(CH_3)_2$ group causes the ^{31}P shift to occur several parts per million upfield of the value for the equatorial isomer. The useful parallel to the steric compression effect of ^{13}C nmr spectroscopy was not drawn in these studies, although more recently the operation of this effect in some trivalent phosphorus cycles has been recognized.[24]

Experimental Section[25]

Synthesis of 1-Substituted Phosphorinanes (1). The procedure employed was essentially that of Grüttner and Wiernik.[26] The di-Grignard reagent was prepared from 1,5-dibromopentane by treating 1 mol of magnesium with 0.44 mol of the dibromide in 500 ml of tetrahydrofuran (THF, dried over calcium hydride). After the exothermic reaction had subsided, the mixture was stirred at room temperature for 3 hr. A solution of 0.5 mol of the appropriate phosphonous dichloride in 300 ml of THF was added dropwise while the reaction was controlled with cooling. The dark color of the Grignard solution lightened and a white solid precipitated. The mixture was stirred overnight (24 hr for the less reactive *tert*-butyl), and then hydrolyzed with 600 ml of saturated NH_4Cl solution, added slowly with cooling. After all solid had been dissolved, the layers were separated. The aqueous layer was extracted with three 200-ml portions of ether; the original organic layer was combined with the other extracts, and drying was performed with $MgSO_4$. Solvent was then stripped off and the residue was distilled. The products with lower molecular weight were pyrophoric and required special care in handling. New phosphines were further characterized by conversion to their sulfides. Data for the compounds prepared are given in Table IV.

Synthesis of Phosphorinane Sulfides (4). Following a reported procedure,[27] the phosphorinane (5 mmol) in 50 ml of benzene was treated with 0.2 g of sulfur, and the mixture was refluxed for 2–3 hr. Unreacted sulfur was removed by filtration of the hot solution. The benzene was evaporated and the residue was recrystallized from petroleum ether or cyclohexane. Sulfides so obtained are listed in Table IV.

***r*-1,*t*-4-Dimethyl-*c*-4-phosphorinanol Sulfide (7a) and *r*-1,*c*-4-Dimethyl-*t*-4-phosphorinanol Sulfide (8a).** 1-Methyl-4-phosphorinanone[28] (3.9 g, 0.03 mol) in 20 ml of THF was added slowly to a solution of 52.2 ml of 2.3 *M* methyllithium in ether and 20 ml of THF. The mixture was refluxed for 24 hr and then cooled (ice bath). Cold water (20 ml) was added cautiously, and the mixture was stirred for 30 min. It was then extracted with ether, and the extract was dried ($MgSO_4$) and distilled. Product (2.5 g, 57%) was collected at 59.5–60.5° (0.6 mm); it consisted of a 2:3 mixture (determined[29] by ^1H and ^{31}P nmr differences) of phosphines **5** and **6**, R = CH_3. The product was placed in 50 ml of benzene and converted to the sulfide as for **2**. The isomeric sulfides were separated by repeated fractional crystallization from benzene. Isomer **8a** was the less soluble. Properties are given in Table V.

***r*-1-Methyl-*t*-4-*tert*-butyl-*c*-4-phosphorinanol Sulfide (7b) and *r*-1-Methyl-4-*c*-*tert*-butyl-*t*-4-phosphorinanol Sulfide (8b).** A cis–trans (2:3) mixture of 1-methyl-4-*tert*-butyl-4-phosphorinanol[29] was converted to the isomeric sulfides by the same procedure as used for **2**. Repeated fractional crystallization from benzene gave the less soluble **8b** in isomerically pure condition; **7b** could not be obtained in pure form, and a 1:1 isomer mixture was used for the spectral study. Properties are given in Table V.

Table IV
Properties of Phosphorinanes and Their Sulfides

A. Phosphorinanes (1)

R	Yield, %[a]	Bp, °C (mm)	Lit. bp, °C (mm)
C_6H_5	32	68–72 (0.2)	119(3.0)[b]
CH_3	38	144–147 (760)	
C_2H_5	20	65–69 (19)	170(760)[b]
i-C_3H_7	24	79–84 (19)	
t-C_4H_9	45	95–99 (20)	

B. Phosphorinane Sulfides (4)

R	Mp, °C	Lit. mp, °C	Formula	Calcd, % C	Calcd, % H	Calcd, % P	Found, % C	Found, % H	Found, % P
C_6H_5	71–73[c]	83,[d] 86[b]	$C_{11}H_{15}PS$	62.83	7.19	14.73	62.61	6.97	14.59
CH_3	49–50	51–52[e]							
C_2H_5	68.5–69.5	67[d]							
i-C_3H_7	147–148.5		$C_8H_{17}PS$	54.51	9.72	17.57	54.39	9.93	17.43
t-C_4H_9	145–147		$C_9H_{19}PS$	56.81	10.06	16.28	57.04	10.30	16.05

[a] General procedure is described in the Experimental Section. [b] K. Issleib and S. Häusler, *Chem. Ber.*, **94**, 113 (1961). [c] This value was obtained on a sample crystallized from petroleum ether[b,d] and also on a sublimed sample. The analysis was satisfactory; the discrepancy with the literature melting point values is unresolved. [d] Reference 27. [e] L. Maier, *Helv. Chim. Acta*, **48**, 133 (1965).

Table V
Properties of 4-Phosphorinanol Sulfides

Registry no.	Compd	Mp, °C	δ PCH_3	J_{PCH}, Hz[a]	δ ^{31}P[b]	Formula	Calcd, % C	Calcd, % H	Calcd, % P	Found, % C	Found, % H	Found, % P
52032-45-8	**7a**	103–105	2.37	13.5	−31.1	$C_7H_{15}OPS$	47.17	8.48	17.38	47.30	8.52	17.37
52032-46-9	**8a**	168–170	2.32	13.0	−28.8	$C_7H_{15}OPS$	47.17	8.48	17.38	47.08	8.55	17.62
52032-47-0	**7b**	*c*	1.79	14.0	−31.9							
52032-48-1	**8b**	146–148	1.75	13.5	−29.4	$C_{10}H_{21}OPS$	54.52	9.61	14.06	54.43	9.78	14.38
52109-47-4	**7c**	190–192	1.79	13.5	−32.0	$C_{12}H_{17}OPS$	59.98	7.13	12.89	59.83	7.10	12.76
52109-48-5	**8c**	182–184	1.82	13.0	−29.1	$C_{12}H_{17}OPS$	59.98	7.13	12.89	59.91	7.25	12.69

[a] In $CDCl_3$ with internal TMS except for **7a** and **8a** (external TMS). [b] Obtained on $CHCl_3$ solutions, except for **7c** and **8c** (methanol). Values were obtained for isomerically pure specimens, except for **7a** and **7b**. [c] Obtained only in admixture with **8b**.

***r*-1-Methyl-*t*-4-phenyl-*c*-4-phosphorinanol Sulfide (7c) and *r*-1-Methyl-*c*-4-phenyl-*t*-4-phosphorinanol Sulfide (8c).** 1-Methyl-4-phenyl-4-phosphorinanol (58% cis, 42% trans)[28] was treated with sulfur as in the synthesis of **2**. Fractional crystallization from benzene gave the less soluble **8c** in pure form. To obtain pure **7c**, the mixture was separated by high-pressure liquid chromatography using a 1:9 v/v mixture of acetonitrile and chloroform on a column of Porasil A. Properties are given in Table V.

The sulfides were also obtained by adding phenylmagnesium bromide [made from 0.8 g (0.03 mol) of magnesium and 4.7 g (0.03 mol) of bromobenzene in 100 ml of THF] to 2.4 g (0.015 mol) of 1-methyl-4-phosphorinanone sulfide[30] in 50 ml of THF. The mixture was refluxed for 4.5 hr, and then hydrolyzed (ice bath) with 10 ml of cold water and 40 ml of 25% NH_4Cl. After standing overnight, the mixture was extracted with chloroform; the extract was dried ($MgSO_4$) and evaporated to leave a crystalline mass. The crystals were washed with a small amount of methanol; the yield was 3.6 g (50%) with the approximate composition 50% **7c** and 50% **8c**.

Registry No.—**5a**, 42565-01-5; **5b**, 33835-61-9; **5c**, 16327-56-3; **6a**, 42565-02-6; **6b**, 33835-62-0; **6c**, 16327-57-4.

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Proton Magnetic Resonance and ^{31}P Nuclear Magnetic Resonance Studies of Substituted Phospholan-3-one 1-Oxides[1]

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A study of the pmr and ^{31}P nmr spectra of a series of 3-phospholanone 1-oxides is reported. Both types of nmr spectra and infrared analysis indicate that an enol–keto tautomerism exists in the solid state and in F_3CCO_2H solution. The following 1-oxides were investigated: 1-benzyl-2-phenylphospholan-3-one, 1-benzyl-2-phenyl-4-methylphospholan-3-one, 1-benzyl-2-phenyl-5-methylphospholan-3-one, 1-benzyl-2-phenyl-4,5-dimethylphospholan-3-one, 1-benzyl-2,5-diphenylphospholan-3-one, and also 4-oxo-2-benzyl-2-phosphabicyclo[3.3.0]octane 2-oxide. Comparison of chemical shifts and coupling constants for HH and $H^{31}P$ with model systems indicates that substituents at C-5 of the phospholan-3-one ring are cis with respect to the P→O group. For substituents at both C-5 and C-4 the relationship with the P→O group is tentatively given as cis and trans, respectively. Methylation of several of these phospholan-3-one 1-oxides gave the corresponding *O*-methyl ethers except for 1-benzyl-2-phenyl-4-methylphospholan-3-one 1-oxide, which afforded 1-benzyl-2-phenyl-2,4-dimethylphospholan-3-one 1-oxide.

As part of a continuing study of the chemistry of saturated, polycyclic carbon–phosphorus heterocycles,[3,4] we have examined the pmr and ^{31}P nmr spectra of several substituted phospholan-3-one 1-oxides.[5] To our knowledge, no systematic spectral analysis of the molecular geometry of these systems has been published. Although our primary objective was to determine the stereochemistry of these products, it was noted that the condensation of dibenzylphosphine oxide with α,β-unsaturated esters in the presence of NaH in THF was dependent upon the concentration of NaH with respect to the yield of the corresponding cyclic 1-oxides **1–7** (Chart I), an observation not recorded in the pioneering work in this area.[5a] As will be noted in Table I, this dependence on concentration of NaH may be of a steric nature, since differences in yield were not observed until the α,β-unsaturated ester was ethyl tiglate, ethyl cinnamate, or carbethoxycyclopentene. The presence of a bulky substituent (R′) of **9** may hinder the conversion of **9** to **10** as proposed originally (Scheme I).[5a] This situation could necessitate the addition of a second equivalent of NaH to convert **9** or **10** to the dianion **11**, which may then cyclize to the desired phospholan-3-one 1-oxide. Although the conditions of the reaction were generally not meticulously optimized for each compound, it is likely with careful manipulation that excellent conversions can be expected with 2 equiv of NaH. Whether or not a dianion such as **11** participates cannot be answered unequivocally, since **12** appears to exist heavily in the enol form even in the

Table I
Yields and Physical Data for the Substituted Phospholan-3-one 1-Oxides

Compd	% yield of 1-oxide: 1 equiv NaH	2 equiv NaH	Mp, °C	Molecular formula	Anal., % (P)	
1[a,b]	49	59	207–208	$C_{17}H_{17}O_2P$	Calcd	10.89
					Found	10.54
2[a]	76	62	216–218	$C_{18}H_{19}O_2P$	Calcd	10.38
					Found	10.19
3	54	49	221.5–223	$C_{18}H_{19}O_2P$	Calcd	10.38
					Found	10.12
4	81	75	181–183	$C_{19}H_{21}O_2P$	Calcd	9.92
					Found	9.74
5[a]	45	89	217–219	$C_{23}H_{21}O_2P$	Calcd	8.59
					Found	8.31
6[a]	67	83	225–226	$C_{20}H_{21}O_2P$	Calcd	9.55
					Found	9.21
7		6[c]	225–226	$C_{23}H_{21}O_2P$	Calcd	8.59
					Found	8.57

[a] These compounds were previously reported in ref 5a. [b] Registry no., 40203-63-2. [c] A yield of 73% of the open-chain compound $(C_6H_5CH_2)_2P(O)CH(C_6H_5)CH(CO_2C_2H_5)_2$ was also obtained. *Anal.* Calcd for $C_{28}H_{31}O_5P$: P, 6.47. Found: P, 6.43. Compound **7** is believed to be the 3 isomer **12b**.