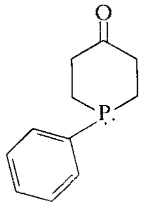
^{13}C and ^{31}P NMR Studies of Configurational and Conformational Effects in 1-Phenyl-4-phosphorinanones and their 1-Selenides

K. Michał Pietrusiewicz
Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Boczna 5, 90-362 Łódź, Poland

Carbon-13 and ^{31}P NMR data are reported for 1-phenyl-4-phosphorinanone and its 1-selenide, as well as for two anancomeric 1-phenyl-3,5-dimethyl-4-phosphorinanones and their 1-selenides. The conformational free energy of the *P*-phenyl substituent in 1-phenyl-4-phosphorinanone is estimated to be $\Delta G° = 0.81$ kcal mol^{-1} (*ca* 80% axial) in chloroform, and this result is consistent with both ^{13}C NMR shielding and coupling data. The γ effects of a single atom substituent on phosphorus are found to be small in the case of selenium; information in the literature indicates significant downfield-shifting γ_e effects due to equatorial oxygen and sulphur substituents in phosphorinanes. In selenides, the shift for the aromatic C-*ipso* carbon in the axial isomer is further downfield than in the equatorial isomer, an observation not precedented in the literature. In the discussion of P–C coupling data a 'second order' Karplus-like relationship is invoked for ^3J(PC), which is dependent both on the dihedral angle and on the orientation of the phosphorus lone pair in phosphines. The one-bond P–C-*ipso* coupling in selenides is identical for all three selenides studied, regardless of the stereochemistry at phosphorus. Similar lack of substantial differentiation is noted for one-bond P–Se coupling. A possible origin of this phenomenon is discussed in terms of diminution of the phosphorus charge contribution to the Fermi contact term. From ^{31}P NMR data a high stereodependence of selenylation shifts is apparent, and greater shifts (by *ca* 20 ppm) are observed when selenium is bound to phosphorus in the more crowded (axial) position. In anancomeric (conformationally biased) phosphines, the isomer with the axial phenyl group has the ^{31}P signal at lower field. This is consistent with observations made previously for rigid 1-phenylphosphorinanes.

Considerable research has been carried out on the stereochemistry of six-membered heterocycles containing phosphorus as the heteroatom (phosphorinanes), and many interesting stereochemical and spectral observations for such systems have already been published.[1] In general, the phosphorinane ring assumes the chair shape. Flattening of this chair at the phosphorus end occurs very easily, especially when an axial substituent on phosphorus has to be accommodated. This flexibility is believed to be largely responsible for the unusual extent to which energy differences between axial and equatorial conformers in phosphorinanes are minimized, which sometimes leads to a situation where the axial form prevails. Such a preference by 0.35, 0.26 and 0.19 kcal mol^{-1}, respectively, was found for 1-methyl-,[2] 1-ethyl-[2] and 1-phenylphosphorinane[2] in solution at room temperature, as well as for 1-phenyl-4,4-dimethoxyphosphorinane[3] in the solid state. On the other hand, for corresponding P^{IV} derivatives, i.e. 1-oxides and 1-sulphides,[4] there is an overwhelming predominance of the conformer with equatorial alkyl[5,6] or phenyl[7] *P*-substituent. Corresponding conformational preferences have also been ascribed to simple 1-alkyl- and 1-phenyl-4-phosphorinanones and their P^{IV} derivatives, both in solution[7,8] and in the solid state,[7,9] although no quantitative evaluations were attempted for any of the compounds studied. In this paper we have addressed the conformational situation in the case of 1-phenyl-4-phosphorinanone (**1**) and its selenide (**2**).



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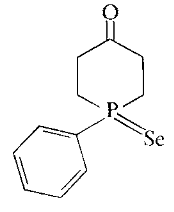

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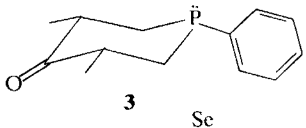
It is well known that NMR parameters, such as chemical shifts and coupling constants, can be employed to calculate conformational equilibria by means of Eliel's equation.[10] To use this approach, room temperature ^{31}P and ^{13}C NMR spectra of **1** and **2** were recorded, together with spectra of the appropriate model compounds, i.e. the two conformationally homogeneous diastereomers **3** and **4** of 1-phenyl-3,5-dimethyl-4-phosphorinanone and their corresponding selenides **5** and **6**.



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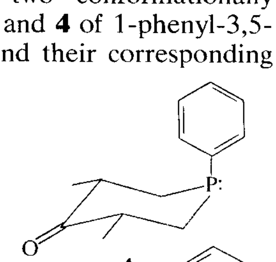

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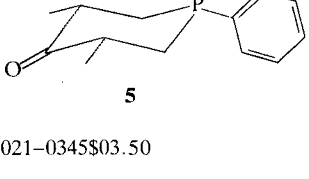

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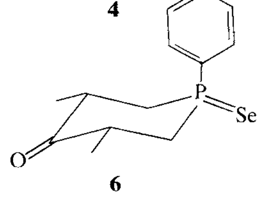

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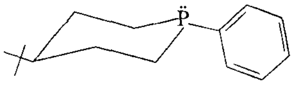
In addition, the conformationally biased compounds **3**–**6** were expected to serve as useful models to probe the generality of certain relationships of ^{31}P and ^{13}C NMR parameters to molecular and electronic structure in six-membered carbon–phosphorus heterocycles. The ^{31}P and ^{13}C NMR parameters for compounds **2**, **5** and **6** represent the first such data collected for selenides derived from cyclic phosphines.

RESULTS AND DISCUSSION

^{13}C NMR chemical shifts

The ^{13}C NMR chemical shifts and assignments for the compounds of interest are given in Table 1.

The data for the rigid phosphines **3** and **4** are presumably indicative of the orientation of the substituent on phosphorus, and reveal noticeable shielding in **4** due to the axial *P*-phenyl group, as expected.[11] The differences in chemical shifts for C-2,6 and C-3,5 in **3** and **4** follow the trends found recently for **7** and **8**[12] and other compounds,[13] but are considerably reduced in magnitude. The upfield shift ($\Delta\delta = 2.1$ ppm) for C-2,6 in going from **3** to **4** is approximately half the $\Delta\delta$ of 4.0 ppm for the corresponding difference between **7** and **8**.[12] The same reduction is found in the differences of the C-3,5 shifts: $\Delta\delta = 1.2$ ppm for **4** vs **3** and 3.5 ppm for **8** vs **7**. These observations suggest markedly less steric compression from axial *P*-phenyl in **4** than in **8**.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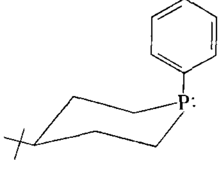
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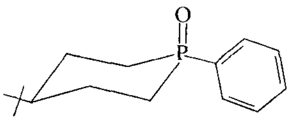
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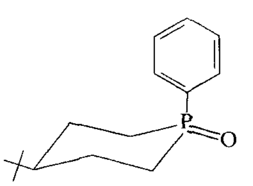
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The carbonyl and methyl carbons in **3** and **4** have similar chemical shifts ($\Delta\delta < 1$ ppm); this implies that there are only minor geometric differences around the carbonyl, and throws doubt on the existence of transannular interactions involving the carbonyl group and either the equatorial or the axial phosphorus lone pair.[7] Moreover, the chemical shifts for the ring carbons in **1** do not suggest any unusual effect.

According to recent findings,[12] the chemical shifts for the carbon atoms in the phenyl group in **3** and **4** might provide some indication of the position of that group. Indeed, C-*ipso* in **3** (equatorial phenyl group) is downfield of that in **4** (axial *P*-phenyl). Again, $\Delta\delta$ (1.7 ppm) was noticeably lower than its value of 3.3 ppm in **7** and **8**,[12] again suggesting less crowding of axial *P*-phenyl in **4** than in **8**. In addition, the signal for C-*ipso* in **1** was nearly the same as in **4** (137.40 vs 137.83 ppm). This implies that **1**, in solution, exists mainly in the conformation with axial *P*-phenyl, a finding already reported by others.[7] Shifts for the remaining aromatic carbons in **1**, **3** and **4** were typical for phenylphosphines.[11]

The ^{13}C NMR chemical shifts for selenides **5** and **6** and their comparison with the shifts for the parent phosphines (**3** and **4**, respectively) will now be discussed. A considerable downfield shift (5.0 ppm) of the C-2,6 signal occurred on introduction of axial selenium into **3** to give **5**. At the same time, the signal for carbons C-3,5 moved upfield by 2.6 ppm, as did that for C-4 (1.3 ppm). An analogous, but larger, downfield shift (7.2 ppm) for C-2,6 was seen in equatorial selenylation of **4** (to give **6**). In this case, however, the shift for C-3,5 changed only slightly and *downfield* (0.5 ppm), whereas increased shielding of C-4 (3.6 ppm) was again noted. These data parallel satisfactorily the usual β and γ effects found for axial and equatorial substituents in six-membered rings;[14] only the δ effects are larger than usual.[14]

Corresponding values relating to shifts accompanying oxidation and sulphurization of conformationally biased phosphorinanes were extracted from the literature and are presented in Table 2 for comparison. Examination of these values disclosed normal β-deshielding effects which are greater for equatorial than for axial substituents, as usual.[14] Similarly, significantly upfield-shifting δ effects, although not observed in cyclohexanes, have been almost uniformly found in phosphorinanes[5,7,8] and have been ascribed to electric field effects.[8] In this context, the small but *downfield-shifting* δ effects accompanying oxidation of 1-phenyl-4-*tert*-butylphosphorinanes are of note.

The most interesting data in Table 2 are the values for the γ_e and γ_a effects. It was recently shown that

Table 1. ^{13}**C NMR chemical shifts**[a] **of phosphorinanones 1, 3 and 4 and their selenides 2, 5 and 6, respectively**

Compound	C-2,6	C-3,5	C-4	CH_3	C-*ipso*	C-o	C-m	C-p
1[b]	23.52	38.46	210.00	—	137.40	129.90	128.60	128.13
2	31.23	37.18	206.29	—	129.55	131.02	129.13	132.35
3	35.90	42.95	211.82	17.26	139.49	130.68	128.50	128.05
4	33.78	41.71	212.72	16.76	137.83	129.35	128.65	127.15
5	40.92	40.79	210.51	16.11	129.50	131.15	128.97	132.35
6	40.98	42.22	208.98	16.28	130.71	129.87	129.42	132.00

[a] Shifts in ppm with respect to TMS.

[b] The ^{13}C NMR spectrum of this compound has been reported;[7] the agreement of the shifts is satisfactory.

Table 2. Substituent effects of single-atom substituents on phosphorus in phosphorinanes

		Substituent effect[a]					
Entry	Substituent	β_e	β_a	γ_e	γ_a	δ_e	δ_a
1[b]	O	6.0	3.1	3.7	−2.5	0.1	0.5
2[c]	S	10.0	3.1	4.2	−3.9	−1.3	−0.5
3[d]	Se	7.2	5.0	0.5	−2.6	−3.6	−1.3

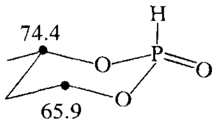
[a] Δδ in ppm; a negative sign indicates an upfield shift. Subscripts e and a describe an effect caused by introduction of a substituent into an equatorial and an axial position, respectively.

[b] Calculated from the ^{13}C NMR spectra of anancomeric 1-phenyl-4-*tert*-butylphosphorinanes **7** and **8** and their 1-oxides **9** and **10**.[12]

[c] Calculated from the ^{13}C NMR spectra of anancomeric 1-methyl-4-hydroxy-4-*tert*-butylphosphorinanes and their 1-sulphides.[5,13]

[d] This study.

the γ-*anti* effect[15] (γ_e effect) is upfield-shifting for substituent atoms more electronegative than carbon,[15] but is converted into a downfield-shifting effect when the intervening atoms are heavily substituted.[16–18] Such an effect could therefore be considered as operating in phosphorinane oxides, sulphides and selenides, for which the γ_e effect is positive and in which the intervening phosphorus atom is, in fact, 'quaternary' (some representative data are given in Table 2). The only available example[19] with 'non-quaternary' P^{IV}, secondary phosphites **11** and **12**, seems to support this reasoning. In **11** the 'normal' upfield-shifting effect of antiperiplanar oxygen[15] apparently equalizes that of the compression shift of the axial P═O in **12**, since shifts for C-4 (74.4 vs 74.8 ppm) and C-6 (65.9 vs 64.6 ppm) are very similar in both compounds.



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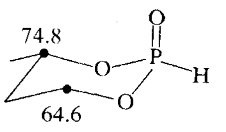

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The size of the γ-*anti* effects (γ_e) observed for O, S and Se atoms (Table 2) does not, however, correlate well with electronegativity unless one assumes that sulphur, as already noted earlier,[20] feigns an electronegativity greater than that recorded in the literature. On the other hand, it is possible that, at least in part, this downfield γ_e shift should be ascribed not to the substituent but to the removal of the lone pair which it binds. It has been shown[21] that the nitrogen lone pair is responsible for a substantial fraction of the shielding of carbons anti-periplanar to it. However, such an effect seems to be relatively unimportant in phosphines since, when the equatorial phosphorus lone pair in **4** is engaged in the formation of a bond with very little ionic character (thus minimizing the development of charge and polar effects) by treatment with selenium to give **6**, only an insignificant downfield shift (0.5 ppm) of C-3,5 occurs.

The values of the γ_a effects of O, S and Se (Table 2) were found to be small, less than the typical γ_a effects of, for example, an axial methyl group in any of several heterocycles, including the *S*-methylthianium system.[14] Clearly, these values do not support previous suggestions of an unusually large γ-shielding effect of an axial single-atom substituent on P in phosphorinanes.[22,23] These suggestions were usually based on the comparison made between pairs of conformationally biased P^{IV} compounds rather than, as in this study, on the comparison of conformationally homogeneous phosphines with their P^{IV} derivatives. Such a comparison was made in an early report,[5] however, only geometric reasons were adduced to explain the derived downfield-shifting γ_e effect of sulphur. Unfortunately, the change from P^{III} to P^{IV} has a number of different consequences, such as expansion of bond lengths and bond angles about phosphorus, and an increase in polarity and decrease in electron density on this atom. None of these changes can, by itself, justify the observed alterations in ^{13}C NMR chemical shifts and, at present, only the overall effect can be considered.

Chemical shifts of C-*ipso* carbons were found to be similar for the selenides **2**, **5** and **6** (Table 1), in contrast[12] to the oxides **9** and **10** where C-*ipso* of the equatorial *P*-phenyl in **9** resonates at lower field (Δδ = 3.3 ppm) than that of the axial *P*-phenyl in **10**. Such a differentiation of axially vs equatorially positioned carbons ascribable to steric factors is commonly observed in various six-membered ring compounds,[14] although some exceptions have already been noted.[14] In this study C-*ipso* of the axial *P*-phenyl in **6**, which is presumably the more crowded isomer, was actually downfield (Δδ = 1.2 ppm) of the corresponding signal in the equatorial *P*-phenyl isomer **5**. To our knowledge, such a crossover has not been previously observed in phosphorinanes. Although this is speculative, one might suspect that the crossover is due to the unusual[2,3,9] disposition of the *P*-phenyl group in **6**, which lowers the steric compression of C-*ipso* at the cost of an increase in repulsions between the *ortho* hydrogens and the equatorial H-2 and H-6 protons. An increased shielding of C-*ortho* in **6** compared with those in **2** and **5** (Table 1) seems to support this suggestion. However, the reciprocal of this effect as felt by C-2,6 is not observed. It is possible that the expected shielding of C-2,6 in **6** may be compensated for by the sizable deshielding associated with the equatorial P═Se group.

The data for **2** (Table 1) parallel very closely those recently published for its P═O and P═S analogues,[7] and do not require additional comment.

^{13}C–^{31}P spin couplings

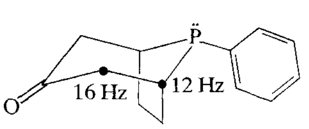
$^nJ(CP)$ coupling constants have proved to be an extremely valuable tool in conformational and configurational assignments, especially in cyclic phosphines, since phosphorus lone pair orientation influences ^{13}C–^{31}P coupling.[11] Phosphorinanes with equatorially oriented lone pairs uniformly exhibit smaller values for one-bond (more negative) and two-bond (less positive) ^{13}C–^{31}P couplings, as well as for three-bond (less positive) coupling to an exocyclic carbon, in comparison with their axial counterparts.[5,12,23] [A negative

Table 3. **^{13}C–^{31}P nuclear spin coupling constants[a] of phosphorinanones 1, 3 and 4 and their selenides 2, 5 and 6, respectively**

Compound	C-2,6[b]	C-3,5	C-4	CH_3	C-*ipso*[b]	C-o	C-*m*	C-p
1	−15.6	c	c	—	−17.6	14.2	3.9	c
2	−45.1	5.9	7.4	—	−70.3	11.0	12.1	3.3
3	−9.8	9.8	c	10.1	−11.7	16.2	c	c
4	−15.6	c	c	c	−19.1	11.8	3.5	c
5	−43.7	4.4	c	14.6	−70.3	10.7	11.8	3.5
6	−42.7	7.3	2.9	13.2	−70.3	11.7	9.7	2.9

[a] Coupling constants in Hz.
[b] A negative sign of the one-bond P–C coupling is assumed; see text.
[c] Not discernible.

sign was ascribed to the one-bond couplings (either endo- or exocyclic) and a positive sign to ^2J(PC) and ^3J(PC) in phosphorinanes.[24]] This regularity was also found to be valid for **3** and **4**, but the differences are much greater in these compounds (Table 3) than those found earlier. Thus, Δ^1J(P, C-2,6) (5.8 Hz) is much greater than that found by interchanging the lone pair position [Δ^1J(P, C-2,6) = 2.7 Hz] in **7** to give **8**.[12] Δ^2J(P, C-3,5) (9.8 Hz) and $\Delta^3J(P, CH_3)$ (10.1 Hz) in **3** and **4** similarly contrast with Δ^2J(P, C-3,5) (5.1 Hz) in **7** and **8**[12] and with $\Delta^3J(P, CH_3)$ (3 Hz) in isomeric 1,3-dimethylphosphorinanes,[23] respectively. Interestingly, even greater differences in ^{31}P–^{13}C coupling [Δ^1J(PC) = 12 Hz and Δ^2J(PC) = 16 Hz] were recorded recently for another pair of ring-substituted (bicyclic) phosphorinanones, **13** and **14**.[25]



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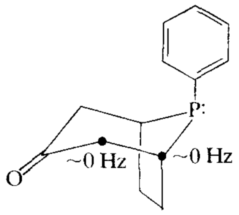

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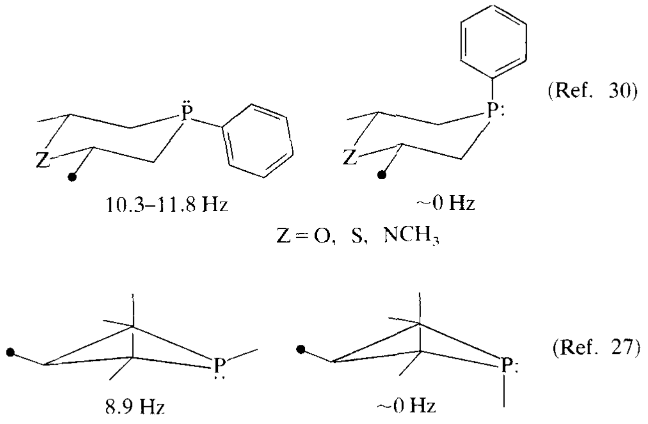
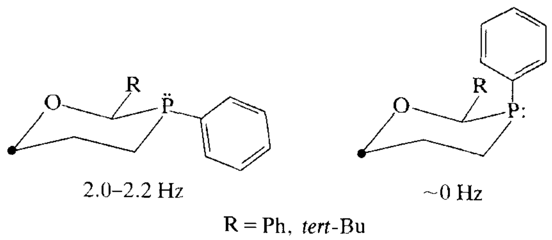
The above comparisons suggest that either ring substitution patterns or the presence of the carbonyl function is responsible for this enhancement of coupling differentiation. The strong dependence of two-bond P–C coupling upon configurational changes at phosphorus found for exocyclic carbons, not only in 1-phenyl-2,2,6,6-tetramethyl-4-phosphorinanone[26] but also in α-methylated phosphetanes[27] and phospholenes,[28] point to the former possibility. [The α-methylated phosphetanes fit into the picture if (and only if) the conformation with axial P—CH_3 and equatorial C-3—CH_3 largely predominates, as assumed by Gray and Cremer.[27] Coupling constants $J(CH_3, P)$ support this predominance: see Ref. 1, pp. 328–383.] However, further studies are required to support this hypothesis.

The most striking feature of the coupling data of **4** (Table 3) is the apparent lack of sizable coupling between phosphorus and the methyl carbons. These carbons are related to ^{31}P by a dihedral angle of approximately 180° in both **3** and **4** but only the methyl signals of **3** are coupled to phosphorus, in reasonable agreement with the Karplus-like relationship derived recently for P^{III} compounds.[29] This observation suggests that the orientation of the phosphorus lone pair is very important in controlling the Karplus-like relationship in phosphines. Seemingly, the dihedral angle between the ^{31}P and ^{13}C-γ nuclei of interest defines a possible range of coupling within which, in turn, the actual magnitude of coupling is governed by the orientation of the lone pair on phosphorus. This is readily seen in cases where the domain of the lone pair influence is large, i.e. when large (*ca* 180°) dihedral angles allow sizable coupling to occur. The literature provides some examples, in addition to our findings for **3** and **4** (Scheme 1). On the other hand, in phosphorinanes in which C-4 is related to ^{31}P by a dihedral angle of approximately 55–60°, the values of ^3J(P, C-4) are usually too small to serve as a probe for the above phenomenon. In one system, however, (Scheme 2) a palpable effect of the phosphorus lone pair disposition on ^3J(PC) was observed.[31] It is thus evident that the maximum three-bond P–C-γ coupling in cyclic phosphines is observed when the ^{31}P and ^{13}C-γ nuclei are *anti* to each other and the phosphorus lone pair occupies an axial position (an '*anti*-perpendicular' orientation). Correspondingly, for the *syn* ^{31}P and ^{13}C-γ nuclei and the axial lone pair disposition (a '*syn*-perpendicular' orientation) the coupling is small but measurable. However, when the phosphorus lone pair is changed to an equatorial position (to an '*anti*-parallel' or '*syn*-parallel' orientation, respectively) the P–C-γ coupling is practically zero in all cases, regardless of the magnitude of the maximum value for the corresponding P/C dihedral angles. (In *cis*- and *trans*-1,3,-dimethylphosphorinanes, coupling of ^{31}P to 3-$^{13}CH_3$ was observed in both isomers, albeit relatively small in magnitude, although greater in the *cis* than in the *trans* isomer. For these



Scheme 1



Scheme 2

compounds, however, some conformational inhomogeneity has to be allowed, as well as some overlapping of signals, which made the assignment not totally definitive.[23]) This argues in favour of the supposition that the orientation of the lone pair on phosphorus is, in fact, of prime importance in controlling the Karplus-type relationship for ^3J(PC) in phosphines. [When the intervening atoms are different from carbon and, more importantly, possess non-bonding electron pairs, a seemingly more complex dependence is developed in which the phosphorus lone pair controls the *syn* and the *anti* P–C coupling by two different modes. See Refs 32 and 33 and also Ref. 14, pp. 231 and 249, for some discussions. See also Ref. 45 for similar trends in ^3J(PH).] Under these circumstances it becomes understandable why this relationship derived recently for P^{III} compounds[29] holds only for systems with freely rotating P^{III} functions in which the lone pair influence is averaged to a large extent.

Couplings to aromatic carbons in **3** and **4** (Table 3) parallel those found previously for the equatorial and the axial *P*-phenyl carbons in **7** and **8**,[12] respectively, providing additional support for the configurational assignments. Again, a smaller (more negative, see above) ^1J(PC) was found in **4**, which possesses an equatorial lone pair on phosphorus, than in **3**.

The coupling pattern for **1** (Table 3) resembles closely that of **4**, implying a correspondence in conformation, i.e. the existence of a predominantly axial phenyl group in **1**.

Analysis of the ^{31}P–^{13}C coupling data for selenides **2**, **5** and **6** (Table 3) revealed only one salient feature. The ^1J(PC) coupling constants for C-*ipso* of the *P*-phenyl ring were found to be identical in all three compounds studied, regardless of their configurational differences at phosphorus. This observation is in sharp contrast to that recently observed for 1-phenyl-4-*tert*-butylphosphorinane 1-oxides **9** and **10**, in which the difference in phosphorus coupling to C-*ipso* of the axial and the equatorial *P*-phenyl was as large as 19.9 Hz.[12] The reasons for this peculiarity are not readily apparent, but some of them are discussed in a later section.

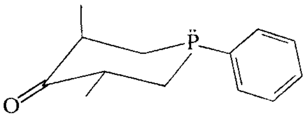
^{31}P NMR chemical shifts

The ^{31}P NMR chemical shifts for the compounds of interest are recorded in Table 4. These data reveal that the ^{31}P NMR anomaly[29] recently found[12] in **7** and **8** recurred in **3** and **4**, placing the axial isomer (**4**) at significantly lower field than the equatorial isomer (**3**). Some distortion of the phosphorinane chair emerged from the ^1H NMR data of **7** and **8** (and their 1-oxides) as the probable origin of this anomaly.[12] However, similar deformations were not clearly suggested for **3** and **4**, either by our previous ^1H NMR study[35] or by the present one. [The exceedingly high sensitivity of the ^{31}P NMR shifts to the steric environment of the observed nucleus has to be kept in mind, however. See Ref. 34.) Moreover, the ^{31}P NMR shift ($\delta = -45.83$ ppm) of **15**, which was present in minute amounts in the mixture of the isomeric 1-phenyl-3,5-dimethyl-4-phosphorinanones,[35] and which is shown below in its predominant conformation,[35] was found to resemble closely that of **3** ($\delta = -43.61$ ppm).

Table 4. ^{31}P NMR chemical shifts and ^1J(P, Se) coupling constants of phosphorinanones 1, 3 and 4 and their selenides 2, 5 and 6, respectively

Compound	1	2	3	4	5	6
$\delta^{31}P^a$	−39.55	19.80	−43.61	−32.53	20.10	10.54
$^1J(P, Se)^b$	—	727.5	—	—	722.7	722.3

^{a} In ppm, downfield from H_3PO_4.
^{b} In Hz.



$\delta^{31}P = -45.83$ ppm
15

Besides providing additional support for the assignments proposed for **3** and **4**, the ^{31}P shift in **15** allows one to make the observation that the additional steric compression exerted on P by the *syn*-axial methyl group induces a normal upfield shift, relative to **3**. Such a normal[36] response of the ^{31}P bearing the equatorial phenyl substituent suggests that the origin of the above-discussed ^{31}P NMR anomaly[34] has to be looked for in the axial rather than in the equatorial isomers, and that this anomaly might tentatively be interpreted as an unusually strong downfield-shifting effect present in phosphorinanes bearing an equatorial lone pair and an axial *P*-phenyl substituent.

The ^{31}P NMR shifts of selenides **5** and **6** are decisively different ($\Delta\delta = 9.6$ ppm), with the equatorial phenyl isomer (**5**) resonating at lower field. The shifts for both flexible compounds **1** and **2** fall, as expected, between the extremes of their rigid counterparts.

Comparison of the ^{31}P NMR data of the phosphines with that of their corresponding selenides (Table 4) discloses large differences in the deshielding accompanying the conversion from P^{III} to P^{IV}. Thus, equatorial selenylation of **4** to give **6** resulted in strong deshielding by 43.1 ppm, but the conversion of **3** into **5** (axial selenylation) produced an even greater deshielding effect of 60.7 ppm. Similarly, introduction of selenium into **1** (to be predominantly axial in **2**) caused deshielding of P by 59.4 ppm and, finally, axial selenylation of **15**, the most crowded isomer, induced a shift to lower field of 62.5 ppm. These values indicate that the selenylation shift in phosphorinanones is apparently highly stereodependent; surprisingly, increased *deshielding* parallels the increase in crowding.

^{31}P–^{77}Se spin coupling

The ^{31}P–^{77}Se coupling constants found for selenides **2**, **5** and **6** are presented in Table 4. These data were expected to provide a basis for the empirical rule recently formulated for one-bond ^{31}P–^{77}Se coupling in 1,3,2-dioxaphosphorinanes[37] [^1J(P, Se) being greater for the equatorially positioned than for the axially positioned selenium] to be extended to C—P heterocycles. Unfortunately, ^1J(P, Se) in the isomeric

Table 5. Variable-temperature ^{31}P NMR spectra of selenides 2, 5 and 6

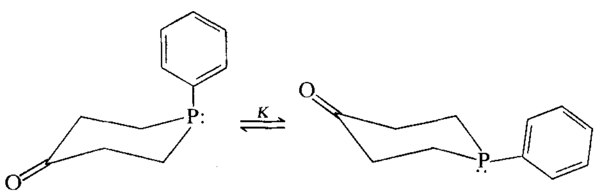
	^{1}J(P, Se)^{a}			δ^{31}P^{b}		
Temperature (°C)	2	5	6	2	5	6
−50	715.3	708.0	703.1	20.55	21.05	10.37
−30	717.8	715.4	703.2	20.65	20.75	10.68
−10	725.0	717.8	713.0	20.24	20.65	10.68
30	727.5	722.7	722.3	19.54	20.04	10.47
50	730.3	725.0	725.1	19.54	19.94	10.47

^{a} In Hz.
^{b} In ppm, downfield from H_3PO_4.

selenides **5** and **6** were practically identical and only slightly smaller (by 5 Hz) than in the flexible analogue **2**. [The same value of 722.7 Hz was also found for ^{1}J(P, Se) in the selenide derived from **15**.] Although coinciding with the equality of the ^{1}J(P, C-*ipso*) coupling constants discussed above, this lack of differentiation in one-bond P–Se coupling in **2**, **5** and **6** is clearly at odds with the differences of 20–55 Hz usually observed in such cases.[37] Variable-temperature ^{31}P NMR measurements revealed (Table 5) that, in general, both ^{1}J(P, Se) and ^{31}P chemical shifts change markedly with temperature, but in a very similar manner for all three selenides studied. This observation seems to preclude any sizable twisting of any one of the phosphorinanone rings in the selenides **2**, **5** and **6**, and simply confirms a known temperature dependence of both ^{1}J(P, Se)[37] and ^{31}P chemical shifts.[36]

In this situation, although steric reasons cannot be definitely ruled out, a possible cause for the observed anomalous coupling pattern of ^{1}J(P, Se) and also of ^{1}J(P, C-*ipso*) (see above) might be associated with the lack of a 'differentiating' factor in the Fermi contact term. (The Fermi term has been ascertained to dominate one-bond coupling[38] and to relate that coupling to the effective nuclear charge.[39]) This factor has been suggested to be the differential axial vs equatorial contribution from the positive charge on phosphorus.[40,41] In view of the absence of any strongly electronegative substituents on phosphorus in **2**, **5** and **6**, little charge development on P can reasonably be assumed; therefore, the above differentiating contribution must, of necessity, become unimportant in these compounds.

Conformational equilibria



1A 1E

The free-energy difference between two conformations of 1-phenyl-4-phosphorinanone (**1**) is given by Eqn (1).

$$\Delta G° = -RT \ln K \qquad (1)$$

The equilibrium constant, *K*, can be calculated from Eqn (2)

$$K = \frac{J_A - J}{J - J_E} \qquad (2)$$

where J_A and J_E are the magnitudes of the coupling constants of the species with an axial and equatorial substituent, respectively, and *J* is the coupling constant measured in the conformationally mobile system exhibiting an average value. It has been demonstrated[42] that in phosphorus-containing six-membered ring systems, coupling between directly bound NMR-active nuclei can be effectively utilized to calculate conformer ratios. The magnitudes of the coupling constants of the individual conformers must be known, however. One can obtain these values by lowering the temperature and slowing down the chair–chair interconversion, or by using anancomeric reference compounds similar to the individual conformers but which cannot interconvert. Theoretically, low-temperature measurements are more accurate; experimentally, however, they are more difficult to perform. In this investigation we have used the method of anancomeric reference compounds to obtain the *K* value, utilizing the one-bond coupling constants, i.e. ^{1}J(P, C-*ipso*) (Table 3). These coupling constants are assumed to be little affected by the 3,5-CH_3 substituents in **3** and **4**.

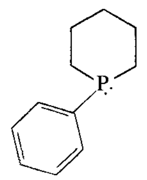
Taking the coupling constant of **1** (−17.6 Hz) as the time average of the two conformers (**1**A and **1**E), a ratio of 0.25 is calculated by Eqn (2) and, consequently, a $\Delta G°$ value of 0.81 kcal mol^{-1} via Eqn (1).

$$K = \frac{-19.1 + 17.6}{-17.6 + 11.7} = 0.25$$

$$\Delta G° = -0.5925 \ln 0.25 = 0.81 \text{ kcal mol}^{-1}$$

These values indicate that at room temperature the conformational mixture of **1** is dominated by the axial form (**1**A) to a large extent (*ca* 80%).

This finding is not surprising when a comparison of **1** with 1-phenylphosphorinane (**16**) is made. Introduction of a carbonyl group on C-4 into **16** (to give **1**) was



16

expected to move the hydrogens at C-3,5 outwards, relieving the *syn*-axial interactions and, thereby, lowering the $-\Delta G°$ value for the *P*-phenyl in **1** in comparison with the $-\Delta G°$ value of −0.19 kcal mol^{-1} of the *P*-phenyl substituent in **16**.[2] Such an effect, called the '4-alkyl ketone effect',[43] has long been known in cyclohexanes and our results are consistent with this interpretation, as well as with the comparison of shielding effects in 1-phenylphosphorinanes and 1-phenyl-4-phosphorinanones (see above). The value of $\Delta G° = 0.81$ kcal mol^{-1} found for **1** needs further confirmation, but may probably be used as a first approximation.

Interestingly, the use of ^{31}P chemical shift values for the calculation of the conformational equilibrium in **1** led to a contradictory result, an anomaly also encountered by others.[42]

Unfortunately, no definitive estimation for the conformational equilibrium in **2** can be made from the data in Tables 1 and 3 since, as discussed before, no differentiation in ^1J(P, C-*ipso*) and ^1J(P, Se) was observed for **2**, **5** and **6**. On the other hand, the similarity of the ^{31}P chemical shift of **2** to that of **5** suggests that the conformer bearing axial selenium strongly predominates in the conformational mixture of **2**, although it is probably not the exclusive isomer.

EXPERIMENTAL

Compounds **1**[44] and **3**–**6**[35] were prepared by known methods. A freshly distilled mixture of phosphines **3** and **4** was used for measurements. Selenides **5** (m.p. 144 °C)[35] and **6** (m.p. 148 °C)[35] were recrystallized (benzene–hexane) before measurements. Selenide **2** was obtained by addition of elemental selenium to **1** in boiling benzene, under nitrogen, for 15 min. Recrystallization of the crude selenide from a benzene–hexane mixture gave pure **2**, m.p. 165 °C, which gave satisfactory NMR and mass spectral data. Proton decoupled ^{13}C and ^{31}P NMR spectra were measured on a JEOL FX-60 (FT) spectrometer at 15.03 and 24.3 MHz, respectively. In addition, a ^{13}C NMR spectrum of **6** was obtained on a Bruker Spectrospin WM-250 operating at 62.89 MHz. Samples were prepared in 10 mm o.d. tubes as 10–15% solutions in $CDCl_3$ with 2–5% TMS as internal reference. The deuterium of the solvent provided the lock signal. ^{31}P–^{77}Se coupling constants were evaluated from the ^{77}Se satellite lines in the ^{31}P NMR spectra of selenides **2**, **5** and **6**.

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