The Conformational Analysis of Saturated Heterocycles. Part LXII.[1] *cis–trans*-Equilibria of 4-Phospha-analogues of 2,6-Dimethylcyclohexanone

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4-Phospha-analogues of 2,6-dimethylcyclohexanones exist in three (isolable) stereoisomeric forms. These have been investigated for the 4-phenylphospha-compound and its oxo-, thioxo-, and selenoxo-derivatives. Equilibrium constants have been determined and corresponding ΔG° differences are compared with those for other hetera-analogues of 2,6-dimethylcyclohexanone.

THE equilibrium constants for the *cis–trans*-equilibria $(A) \rightleftharpoons (B)$ for 4-hetera-2,6-dimethylcyclohexanones (2)—(6) with different Z groups allow comparisons of the relative strengths of methyl–Z interactions. Systems previously investigated include Z = CH_2 (1),[2,3] NBu^t (2),[4] N-aryl (3),[5] O (4),[6] S (5),[6] and SO_2 (6).[6] The results were interpreted in terms of 1,3-diaxial interactions (E) between Z and the axial methyl group in the *trans*-isomer (*B*). Thus ($E_{repulsive} - E_{attractive}$) in (*B*) is less for Z = O or NBu^t than for CH_2 and is less again for Z = S or SO_2. These conclusions appear to hold for a variety of structures and conditions; the equilibrium for Z = CH_2 is relatively insensitive to solvent [6] and that for Z = N-aryl not particularly sensitive to small changes in hybridisation at nitrogen.[5] The difference between CH_2 (1*B*) and S (5*B*) or SO_2 (6*B*) is readily rationalised in terms of the longer C–S bond distances in those molecules. The results for the equilibria for (1),

(*A*) (*B*)

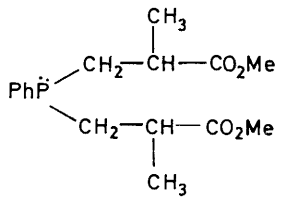
(1) Z = CH_2
(2) Z = NBu^t
(3) Z = NAr
(4) Z = O
(5) Z = S
(6) Z = SO_2

(7) Z = PPh
(8) Z = P(O)Ph
(9) Z = P(S)Ph
(10) Z = P(Se)Ph

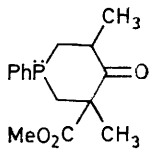
(2), and (4) must be ascribed to a smaller interaction of the methyl group with an oxygen or nitrogen lone pair than with a hydrogen atom. This arises either from diminished repulsion or enhanced attraction, or a combination of both.

We have now examined systems where Z corresponds to a phosphorus grouping: Z = PPh (7) provides a direct comparison with the corresponding nitrogen, oxygen, and sulphur systems, and Z = P(O)Ph (8), P(S)Ph (9), and P(Se)Ph (10) permit examination of methyl interactions with groups other than H or lone pair.

Preparation of Compounds.—Phenylphosphine [7] was converted [8] by methyl methacrylate into the bis(methyl ester) (11) as a mixture of equal amounts of (±)- and



(11)



(12)

meso-forms. Cyclisation [(11) ⟶ (12)] and hydrolysis and decarboxylation then gave the cyclic ketone (7). Oxidation of (7) with hydrogen peroxide, and reaction of (7) with sulphur or selenium gave the corresponding oxo-, thioxo-, and selenoxo-analogues (8)—(10).

Equilibration of Compounds.—As previously,[4-6] equilibration was accomplished simultaneously with deuteriation α to the carbonyl group (to simplify the interpretation of the n.m.r. spectra) by treatment with dilute sodium deuterioxide in deuterium oxide–dioxan. This solvent system was chosen to expedite equilibration and avoid side reactions, *e.g.* oxidation of (7), resulting from prolonged exposure. Progress of the exchange was followed by n.m.r. and the equilibrations were performed at 37°.

EXPERIMENTAL

N.m.r. spectra were recorded on a Varian HA-100 spectrometer with dioxan as internal lock. I.r. spectra were measured with a Perkin-Elmer PE125 spectrophotometer.

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[5] M. D. Brown, M. J. Cook, G. Desimoni, and A. R. Katritzky, *Tetrahedron*, 1970, **26**, 5281.
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[8] B. A. Arbuzov, G. M. Vinokurova, and I. A. Perfil'eva, *Doklady Akad. Nauk. S.S.S.R.*, 1959, **127**, 1217 (*Chem. Abs.*, 1960, **54**, 1377g).

Equilibration: General Procedure.—AnalaR dioxan was distilled prior to use and kept over molecular sieves. The phosphorinanone (20—40 mg) was dissolved in dioxan (1·0 ml) and deuterium oxide (0·05 ml) in an n.m.r. tube and the n.m.r. spectrum recorded. Sodium deuterioxide solution (6%; 0·1 ml) was added and the mixture kept at 37° with occasional shaking. After 6 h the partially immiscible aqueous layer was separated and the procedure repeated with fresh sodium deuterioxide (0·1 ml). The equilibration was monitored by n.m.r. and in a typical run was complete after *ca.* 10 h. The aqueous layer was removed and the organic layer used for the n.m.r. analysis.

3,5-*Dimethyl*-1-*phenylphosphorinan*-4-*one.*— Bis-(2-methoxycarbonylpropyl)phenylphosphine (15·5 g; 0·05 mol) in xylene (100 ml) was added dropwise to a stirred suspension of sodium (1·2 g, 0·05 mol) in xylene under nitrogen and the mixture was heated under reflux for 4 h. The whole was cooled, washed with water (3 × 150 ml), and dried ($MgSO_4$). The solvent was distilled off at 20 mmHg and the residual oil heated under reflux for 3 h with 4N-hydrochloric acid (250 ml). The solution was neutralised at 0° with 5N-sodium hydroxide and extracted with chloroform (3 × 100 ml). The dried ($MgSO_4$) extract was distilled to yield the *phosphorinanone* (1·9 g, 17·8%) as an oil, b.p. 103° at 0·01 mmHg, 120° at 0·3 mmHg, 145° at 2 mmHg, n_D^{20} 1·5723 (Found: C, 71·1; H, 7·3. $C_{13}H_{17}OP$ requires C, 70·9; H, 7·7%).

Preparative t.l.c. [silica gel; ethyl acetate–chloroform (3 : 7)] under nitrogen did not resolve the isomers (n.m.r. data given in Table 1).

After equilibration with H–D exchange the phosphorinanone gave a mixture of components exhibiting the n.m.r. absorptions given in Table 2.

3,5-*Dimethyl*-1-*phenylphosphorinan*-1,4-*dione* (8).—Hydrogen peroxide (50%; 2 g) was added dropwise with stirring to 3,5-dimethyl-1-phenylphosphorinan-4-one (2·14 g, 0·0097 mol) in $CHCl_3$ (40 ml) at 0—5°. An exothermic reaction resulted. The mixture was stirred for 2 h at room temperature, diluted with $CHCl_3$ (100 ml), washed with ferrous sulphate solution (5%; 3 × 20 ml) and water (3 × 20 ml), and then dried ($MgSO_4$). The solvent was evaporated and the residue recrystallised from diethyl ether to give the *oxide* (0·6 g, 26%) as needles, m.p. 124—126° (Found: C, 66·1; H, 7·4. $C_{13}H_{17}O_2P$ requires C, 66·1; H, 7·3%).

3,5-Dimethyl-1-phenylphosphorinan-1,4-dione (8) was found by t.l.c. to be largely a single component; a minor second compound was shown by n.m.r. to be an isomer.

Equilibration with H–D exchange by the general procedure converted the dione into a mixture of three components with the n.m.r. methyl absorptions given in Table 2.

3,5-*Dimethyl*-1-*phenyl*-1-*thioxophosphorinan*-4-*ones* (9).—Freshly sublimed sulphur (0·64 g, 0·02 mol) was added gradually with stirring to 3,5-dimethyl-1-phenylphosphorinan-4-one (2·5 g, 0·013 mol) in benzene (20 ml). When the exothermic reaction subsided, the reaction mixture was heated under reflux for 15 min and then cooled to 0°. The excess of sulphur was filtered off. Benzene was evaporated at 20 mmHg and the residue recrystallised from methanol to give a mixture of the isomeric sulphides (1·8 g, 63%) as needles, m.p. 100—104° (Found: C, 62·2; H, 6·3. Calc. for $C_{13}H_{17}OPS$: C, 61·9; H, 6·7%).

Preparative t.l.c. [silica gel; ethyl acetate–chloroform (3 : 7)] gave two principal components (9*a*), m.p. 114—116°, R_F 0·72, and (9*d*), m.p. 142—144°, R_F 0·66. Isomer (9*d*), isolated in small quantity only, was shown by t.l.c. and n.m.r. to be contaminated with *ca.* 10% of isomer (9*a*) which could not be removed by recrystallisation. N.m.r. data for the *C*-methyl groups are given in Table 1.

Equilibration with H–D exchange by the general procedure converted both (9*a* and *d*) into mixtures with identical t.l.c. and n.m.r. spectra (Table 2).

3,5-*Dimethyl*-1-*phenyl*-1-*selenoxophosphorinan*-4-*ones* (10).—Selenium (0·79 g, 0·01 mol) was added gradually with stirring to 3,5-dimethyl-1-phenylphosphorinan-4-one (1·0 g, 0·0045 mol) in dry methanol (7 ml). When the exothermic reaction ceased the whole was heated under reflux for 15 min and then cooled to 0°. The excess of selenium was filtered off. Methanol was evaporated under reduced

TABLE 1

Physical properties and n.m.r. data for 3,5-dimethyl-1-phenylphosphorinan-4-one derivatives

Compound no.	Substituent at phosphorus	Configuration	M.p. (°C)	R_F	δ_{CH_3}	J_H/Hz	J_P/Hz
(10*a*)	Se	*cis-ax*-Se	144—145	0·76	1·09	6·5	2·2
(10*d*)	Se	*cis-eq*-Se	148—150	0·71	1·01	6·0	2·4
(9*a*)	S	*cis-ax*-S	114—116	0·72	1·07	6·4	2·2
(9*d*)	S	*cis-eq*-S	142—144	0·66	1·01	6·0	2·4
(8*a*)	O	*cis-ax*-O	126—127		1·09	6·4	2·2
(7)	Unsubstituted	Mixture of isomers	B.p 120 at 0·3 mmHg		0·98 1·08 1·24	6·4 6·5	~0 ~0

TABLE 2

Equilibrium data for 3,5-dimethyl-1-phenylphosphorinan-4-one derivatives

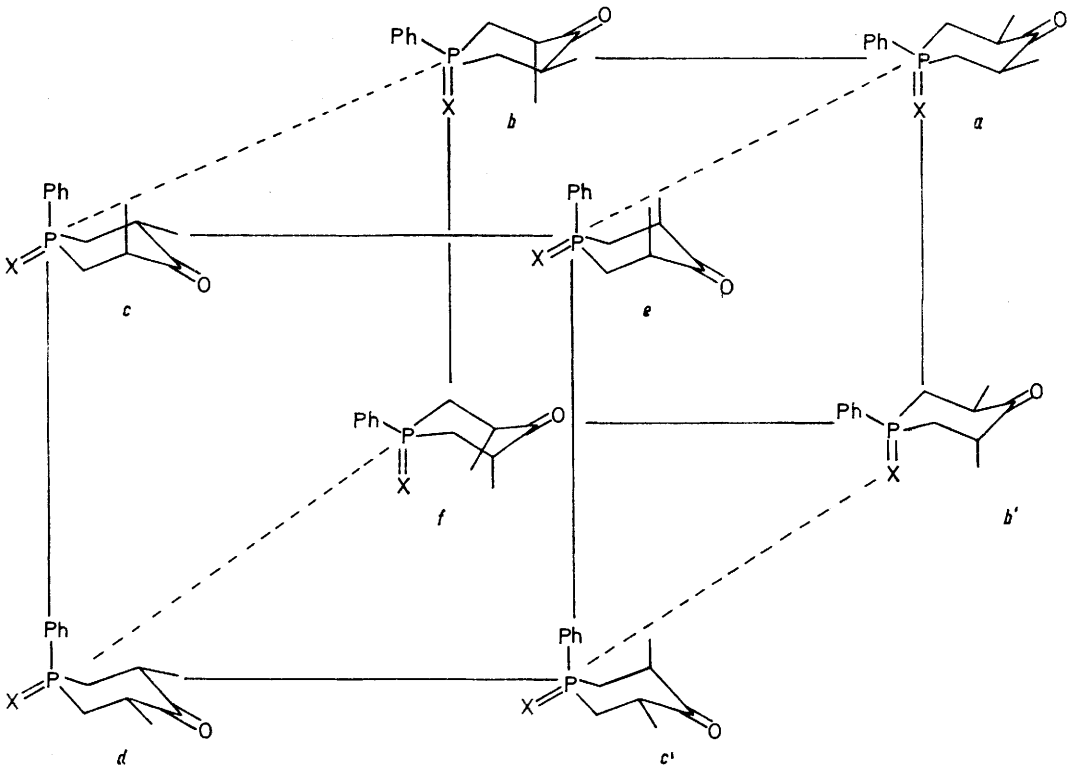
	CH_3 Chemical shifts (δ)			Integrated areas (%)			*trans* (*b* ⇌ *c*) ⇌ *cis* (*a*)		*cis* (*d*) ⇌ *cis* (*a*)	
Compound no.	*cis*(*a*)	*cis*(*d*)	*trans* (*b* ⇌ *c*)	*cis* (*a*)	*cis* (*d*)	*trans* (*b* ⇌ *c*)	*K*	$-\Delta G°_{310}$/ kcal mol^{-1}	*K*	$-\Delta G°_{310}$/ kcal mol^{-1}
(10)	1·06	1·00	1·06,* 1·15	81	6	13	6·2	1·08	13·5	1·54
(9)	1·05	0·99	1·05,* 1·14	81·5	5·5	13	6·3	1·13	14·8	1·66
(8)	1·06	1·03	1·12, 1·22	82	6	12	6·8	1·14	13·7	1·55
(7)	1·03	0·92	1·12, 1·22	65	25	10	6·5	1·11	2·6	0·57

* Peak assumed to lie under the *cis*(*a*) peak, see text.

pressure and the residue recrystallised once from ethanol to give a mixture of the isomeric selenides (1 g, 77%) as needles, m.p. 128—131° (Found: C, 52·6; H, 5·3. Calc. for $C_{13}H_{17}OPSe$: C, 52·1; H, 5·6%).

Preparative t.l.c. [silica gel; ethyl acetate–chloroform (3 : 7)] gave two principal components (10*a*), m.p. 144—145°, R_F 0·76, and (10*d*), m.p. 148—150°, R_F 0·71, with the *C*-methyl n.m.r. data shown in Table 1. In the i.r. spectra (*ca.* 5% in CS_2) (10*a* and *d*) showed bands at 502 and 574 cm^{-1} respectively.

Equilibration with H–D exchange by the general procedure converted both (10*a* and *d*) into mixtures with identical n.m.r. spectra. The *C*-methyl chemical shifts observed for the mixtures are given in Table 2. The equilibrated mixtures each exhibited a prominent i.r. absorption at *ca.* 499 cm^{-1} with only minor absorption at 574 cm^{-1}.



SCHEME Conformations of the phosphorinanones (7)—(10). Conformations interconvertible by ring inversion are connected by dotted lines; those interconvertible by methyl inversion are connected by solid lines

RESULTS

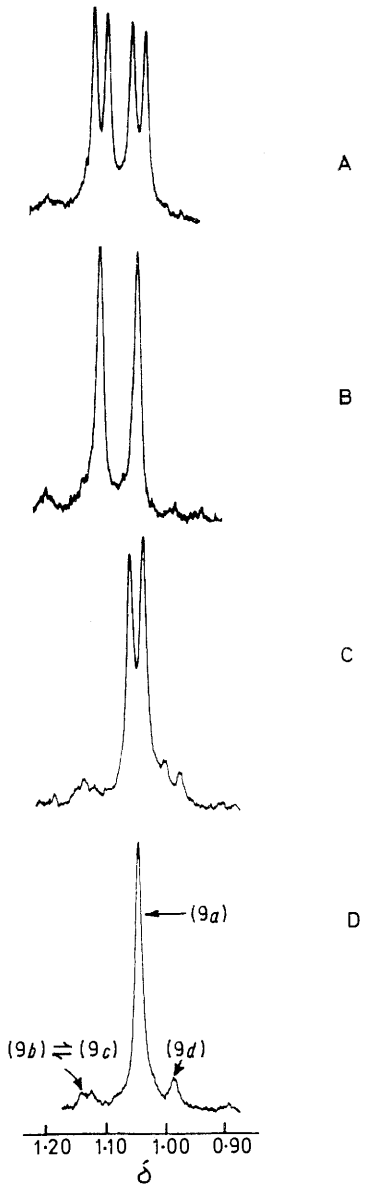
Equilibration of the phosphorinanones (7)—(10) interconverts each between eight possible chair forms (Scheme). Four of these are *cis*-forms where *cis* refers to the arrangement of the 3- and 5-methyl groups: *a* and *d* possess two equatorial methyl groups, but differ in their configuration at phosphorus; the ring inverted ' diaxial ' *cis*-forms *e* and *f* are energetically unfavourable because of severe methyl–methyl interactions and do not contribute significantly. The four *trans*-forms occur in enantiomeric pairs, *b*,*b'* and *c*,*c'*, each pair differing in the configuration at phosphorus. Conformers *b* and *c* (and also their enantiomers *b'* and *c'*) rapidly equilibrate through ring inversion and are expected to give rise to time-averaged n.m.r. spectra at room temperature. Hence, at ambient temperature, three separate n.m.r. signals are expected: from *cis*-(*a*), *cis*-(*d*), and the *trans*-(*b* ⇌ *c*) forms.

The assignment of the equilibrium proportions was carried out by n.m.r. analysis of the methyl resonances. Isomer *a* shows a single resonance for its equivalent methyl groups and so does *d*. The *trans*-isomer pair *b*,*c* shows two methyl resonances of equal area as the two methyl groups are here in different environments, but *b* and *c* are time-averaged. The *trans*-isomer pair *b'*,*c'* is a mirror image of *b*,*c*. The methyl resonances are split by coupling to the α-hydrogen atoms (*ca.* 6·5 Hz) and to the phosphorus atom (*ca.* 0—2·5 Hz depending on the substitution and configuration at phosphorus). These splittings were identified, and the spectra simplified, by deuteriation and by decoupling at the ^{31}P frequency. The Figure illustrates n.m.r. spectra for the equilibration of the phosphorinanone (9*a*). Distinction between the individual *cis*-isomers *a* and *d* was assisted by i.r. analysis.

Selenoxophosphorinanone (10).—The 1-selenoxophosphorinan-4-one (10) was separated by t.l.c. into two isomers, m.p.s 144—145 and 148—150°, each exhibiting only one methyl resonance. These isomers were thus the two possible *cis*-forms (10*a* and *d*). The original isomer mixture showed moderately strong i.r. absorptions at 574 and 502 cm^{-1} and these absorptions formed the only major difference from the i.r. spectra of the corresponding phosphine (7). In this region of the phosphorus–selenium stretching vibration,[9] the individual isomers (10*a* and *d*)

[9] D. E. C. Corbridge in ' Topics in Phosphorus Chemistry,' eds. M. Grayson and E. J. Griffith, Wiley, New York, 1969, vol. 6, p. 235.

exhibited only one of the bands quoted; they are therefore due to axial and equatorial P=Se groups. Little has been reported on the effect of the configuration on ν(P=Se); we applied the empirical rule [10] that stretching frequencies of equatorial substituents are higher than those of their axial



Equilibration of 3,5-dimethyl-1-phenyl-1-thioxophosphorinan-4-one (9*a*). N.m.r. spectra of C–Me region: A, before equilibration; B, spectrum A with ^{31}P decoupling; C, after equilibration and H–D exchange; D, spectrum C with ^{31}P decoupling

analogues. This is consistent with the established correlations with the phosphoryl band of 1,3,2-dioxaphosphorinan-2-ones [11] for a variety of *P*-substituents. Configuration (10*a*) is therefore assigned to the isomer with m.p. 144—145° with the absorption at 502 cm^{-1} and (10*d*) to that with m.p. 148—150° absorbing at 574 cm^{-1}.

Upon equilibration, (10*a* and *d*) each gave rise to the same mixture of three compounds. The principal component exhibited a single methyl resonance establishing it as one of the *cis*-forms. I.r. and t.l.c. analysis of the mixture confirmed its identity with (10*a*). The small difference in the chemical shift of the methyl resonance before and after equilibration (see Table 1) is attributed to the added sodium deuterioxide. Assuming this effect to be similar for each of the isomers, the peak upfield from the principal component is assigned to (10*d*) and the remaining resonance to part of the spectrum of the *trans*-isomer (10*b* ⇌ *c*). A peak of area equal to that of the signal at δ *ca.* 1·15 is assumed to fall under the major component and form the other half of the spectrum of (10*b* ⇌ *c*). In the oxide (8), the coincidence of these two signals does not occur and the two peaks belonging to (8*b* ⇌ *c*) are both clearly seen. Equilibrium constants and $\Delta G°$ data are given in Table 2.

Thioxophosphorinanone (9).—The two isomers separated from the 1-thioxophosphorinan-4-one (9) showed single n.m.r. methyl absorptions and therefore correspond to the two possible *cis* forms (9*a* and *d*). The i.r. spectrum of the mixture showed several bands between 860 and 535 cm^{-1} (not present in the unsubstituted phosphines) which is the phosphorus–sulphur stretching vibration region.[9] Insufficient data on P=S i.r. bands, and the multiplicity of additional bands observed for the separate isomers, preclude unambiguous assignment of the configurations of the two *cis*-forms. However the similarity of the n.m.r. data of the isomers of the thioxo-compounds (9) with the selenoxo-analogues (10*a* and *d*), and the order of the t.l.c. R_F values, imply that the compound, m.p. 114—116°, with chemical shift δ 1·07 is (9*a*) with an axial P=S group, and the compound with m.p. 142—144° is (9*d*).

Equilibration of the thioxophosphorinanones (9*a* and *d*) yielded identical three-component mixtures. N.m.r. and t.l.c. confirmed that the principal component in each case was (9*a*). The parallel behaviour of the thioxo- (9) and the selenoxo-compounds (10) supports the tentative structural assignments of the isomers of the thioxo-series (9). The minor peak at high field was attributed to the axial phenyl *cis*-isomer (9*d*) as above and the low field resonances at δ 1·14 and 1·05 (assumed hidden by the principal peak) to the *trans*-thioxophosphorinanone (9*b* ⇌ *c*). Equilibrium constants and $\Delta G°$ data are given in Table 2.

Phosphorinandione (8).—The phosphorinan-1,4-dione (8) as prepared exhibited a single n.m.r. methyl resonance consistent with either (8*a* or *d*), and a strong band at 1204 cm^{-1} for the ν(P=O).[9] A mixture of isomers of this isolated compound, present in the crude oxidation mixture from the phosphine (7), showed the same i.r. band and a number of less intense absorptions in the same region but all at higher frequency. This suggests that the phosphorinandione isolated has the phosphoryl group axial (8*a*).

As in the previous cases, equilibration of (8*a*) yielded three components, the principal one of which was identical by n.m.r., t.l.c., and i.r. with the starting isomer (8*a*). The two downfield peaks are assigned to the *trans*-form (8*b* ⇌ *c*) and the upfield peak to the remaining *cis*-compound with the phenyl group axial (8*d*). Equilibrium constants and $\Delta G°$ data are given in Table 2.

Phosphorinanone (7).—T.l.c. of the phosphorinanone (7) in a number of solvent systems did not resolve the mixture of isomers. The isomer mixture (7) showed two major methyl resonances in the n.m.r. at δ 0·98 and 1·08; the

[10] M. Larnaudie, *J. Phys. Radiation*, 1954, **15**, 650 (*Chem. Abs.*, 1958, **52**, 17,959h).

[11] J.-P. Majoral and J. Navech, *Spectrochim. Acta*, 1972, **28A**, 2247.

resonances were of unequal area (42 : 58 respectively) and therefore cannot be assigned to the *trans*-form (*7b* ⇌ *c*). Provided that no overlap of peaks occurs, it follows that the major resonances arise from the two *cis*-configurations (*7a* and *d*), by analogy with the preceding compounds. A minor doublet at δ 1·24 is assigned to the *trans*-isomer (*7b* ⇌ *c*), the other methyl resonance being assumed to be obscured by the large peak at δ 1·08. The lack of coupling to phosphorus of the methyl groups of all three phosphorinanone isomers is a notable difference from the pentavalent derivatives (8)—(10), but such effects have been encountered frequently in related systems.[12]

Upon equilibration and H–D exchange, phosphorinanone (7) gave rise to a mixture of compounds exhibiting four resonances at δ 0·92, 1·03, 1·12, and 1·22. The two peaks of highest chemical shift are of small but equal intensity and are assigned to the *trans*-form (*7b* ⇌ *c*). The assignment of structures to the two principal components is tentative and is based on analogy with the substituted derivatives (8)—(10). Thus the resonance at δ 1·03 is assigned to (*7a*) and the higher field peak at δ 0·92 to (*7d*). This assumes that the relative effects on forms *a* and *d* of changing X from lone pair to O, S, or Se are similar; since the methyl groups are far from the site of change this is probably the case. Equilibrium constants and $\Delta G°$ data are given in Table 2.

DISCUSSION

The nature of the phosphorus substituent in the substituted phosphorinanones (8)—(10) has little effect on the equilibration behaviour (Table 2). Consideration of interactions in models of the derivatives (8)—(10) reveals the favoured conformer *a* to be relatively sterically unhindered. The axial position is occupied by the P=X group, a configuration established as favoured by many similar polar groups in other ring systems, *e.g.* the *N*-oxide bond of *N*-methylmorpholine *N*-oxide,[13] the P=O bond of 2-phenyl-1,3,2-dioxaphosphorinan-2-one,[14] the sulphinyl oxygen of thian 1-oxide,[15] and Se=O in selenane derivatives.[16]

Conformer *d* on the other hand experiences considerable interaction between the phenyl ring and the axial protons at C-3 and C-5, rendering it appreciably less favourable. In 1-phenylphosphorinan-4-one [17] and its dimethyl acetal,[18] *X*-ray crystallography has revealed the *P*-phenyl group to be axial. Such a conformation, however, possesses considerable overcrowding of the phenyl group with the β-diaxial protons, and this is relieved by flattening of the ring at phosphorus. Whether such a conformation persists as the most favourable in solution is unknown. However, recent ^{31}P n.m.r. solution studies of 1-methylphosphorinan [19] reveal an equatorial preference for the *P*-methyl group at low temperature but a 56% axial preference at room temperature. The temperature dependence of the conformational equilibrium, and hence the axial preference at 25°, arises from a combination of a small $\Delta H°$ and non-negligible entropy differences. In conformation *d* of the substituted phosphorinanones (8)—(10), strain relief by flattening at phosphorus is severely restricted by the valency of the phosphorus atom and we conclude that *d* is expected to be a sterically crowded isomer.

Conformations *b* and *c* are in rapid equilibrium at room temperature by ring inversion. While *b* suffers the usual interactions of an axial methyl group, possibly influenced to some extent by unknown interactions with the P=X group, conformation *c* has a severely crowded β-diaxial methyl–phenyl arrangement and should not contribute greatly to the equilibrium. On time-average, the n.m.r. spectrum of *b* ⇌ *c* will resemble conformation *b* alone. For this reason it is not surprising that the upfield (equatorial) methyl resonance of *b* frequently coincides with the resonances of conformer *a*.

We conclude from these considerations that in the substituted phosphorinanones (8)—(10), *a* is the most favoured isomer. Conformer *b*, the principal contributor to the *trans*-form *b* ⇌ *c* is less stable than *a* owing largely to β-diaxial methyl–hydrogen interactions, and *d* is the least favoured of the measurably populated forms. These conclusions are borne out in the quantitative data (Table 2).

Replacement of PO, PS, or PSe by P to give the phosphorinanone (7) should have little effect on the *cis–trans* equilibrium *a* ⇌ *b* because of the long [17] P–C bond lengths (1·84 Å) [*cf.* the equilibrium (*A*) ⇌ (*B*) for Z = S and SO_2 (Table 3) where oxidation at sulphur has negligible effect [6]]. However isomer *d* should now be more appreciably populated since the trivalent

TABLE 3

Summary of data for the equilibrium (*A*) ⇌ (*B*)

Z	$\Delta G°$/ kcal mol^{-1}	$\Delta H°$/ kcal mol^{-1}	Reference
CH_2	1·50	1·90	*a*
NBu^t	0·93	1·33	*b*
N-aryl	0·9—1·1	1·3—1·5	*c*
O	0·92	1·32	*a*
S	0·61—0·76	1·01—1·16	*a*
SO_2	0·65	1·05	*a*
Compound			
(10*a*)	1·08	1·5—1·7	*d*
(9*a*)	1·13	1·6—1·8	*d*
(8*a*)	1·14	1·6—1·8	*d*
(7*a*)	1·11	1·5—1·7	*d*

[a] Ref. 6. [b] Ref. 4. [c] Ref. 5. [d] Current work.

[12] G. Mavel in 'Progress in Nuclear Magnetic Resonance Spectroscopy,' eds. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Pergamon, Oxford, 1966, vol. 1, pp. 251—373.

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phosphorus pyramid may undergo flattening to relieve steric compression. These predictions are borne out in the results (Table 2).

Table 3 summarises the available data on the equilibrium $(A) \rightleftharpoons (B)$ for a number of different Z groups. Assuming conformation *c* to make only small contribution to the *trans*-form, equilibrium $(A) \rightleftharpoons (B)$ [when Z = P(*ax*X)*eq*Ph] is approximated by equilibrium $a \rightleftharpoons b + c$. The equilibrium $(A) \rightleftharpoons (B)$ for the alternative configuration at phosphorus is not measurable at room temperature.

Comparison of the $\Delta H°$ values in Table 3 is complicated by uncertainties for the unsymmetrical phosphorus compounds. For the Z groups CH_2, NR, O, S, and SO_2, the ΔS_{mixing} value is unambiguously $R \ln Z$ cal mol^{-1} K^{-1}. However, for the unsymmetrical phosphorus groups, this value is increased significantly for even small populations (*ca.* 5%) of the alternative invertomer of (*B*), *i.e.* of forms *c*, hence the ranges shown for $\Delta H°$ in Table 3. Similarly, small contributions of boat conformers to the *cis*-form *d* could contribute significant entropy of mixing and thus influence the measured $\Delta G°_{310}$ values.

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