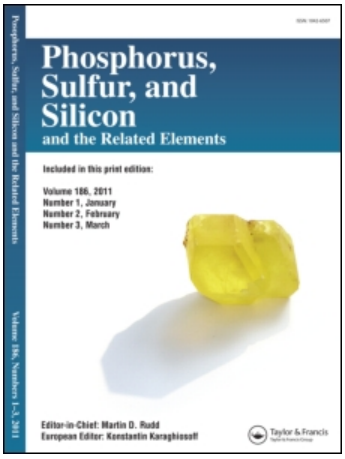

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

ORGANOPHOSPHORUS INTERMEDIATES XI.[1] PREPARATION AND STEREOCHEMISTRY OF P-PHENYLATED 1,3-DIPHOSPHOLANE, 1,3- AND 1,4-DIPHOSPHORINANES, 194-DIPHOSPHEPANE AND 1,5-DIPHOSPHOCANE[2]

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To cite this Article Brooks, Peter J. , Gallagher, Michael J. , Sarroff, Adrian and Bowyer, Michael(1989) 'ORGANOPHOSPHORUS INTERMEDIATES XI.[1] PREPARATION AND STEREOCHEMISTRY OF P-PHENYLATED 1,3-DIPHOSPHOLANE, 1,3- AND 1,4-DIPHOSPHORINANES, 194-DIPHOSPHEPANE AND 1,5-DIPHOSPHOCANE[2]', Phosphorus, Sulfur, and Silicon and the Related Elements, 44: 3, 235 — 247
To link to this Article: DOI: 10.1080/10426508908040614
URL: http://dx.doi.org/10.1080/10426508908040614

Phosphorus, Sulfur, and Silicon, 1989, Vol. 44, pp. 235–247
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ORGANOPHOSPHORUS INTERMEDIATES XI.[1] PREPARATION AND STEREOCHEMISTRY OF P-PHENYLATED 1,3-DIPHOSPHOLANE, 1,3- AND 1,4-DIPHOSPHORINANES, 1,4-DIPHOSPHEPANE AND 1,5-DIPHOSPHOCANE[2]

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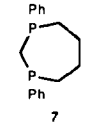
(Received November 14, 1988)

The eponymous 5-, 6- and seven-membered diphosphorous heterocycles have been prepared by alkylating diphosphides with α,ω-dihalides and separated into stereoisomers. One isomer of the 1,5-diphosphocane has been obtained by reduction of the dioxide with trichlorosilane. Stereochemistry is assigned on the basis of ^{1}H, ^{13}C, ^{31}P nmr, infrared and mass spectral studies and the X-ray structure of the *trans*-1,4-diphosphorinane. Thermal inversion studies on the 5-, 6- and 7-membered heterocycles are described.

Key words: Heterocycles; diphosphines; stereochemistry; nmr; inversion.

INTRODUCTION

We have previously described[3] the generation and some properties of the diphosphides $PhPR(CH_2)_nRPPh$(**1**, R = Li, n = 2–5), obtained by cleavage of the corresponding **1** (R = Ph) with lithium and now report their use in the synthesis of heterocyclic diphosphines **2–5**. An alternative route to the eight-membered diphosphine **6** is also described. Our interest in these diphosphines stems from their potential uses as novel complexing agents and also as convenient intermediates in the synthesis of molecules with phosphorus bridgehead atoms for stereochemical and mechanistic studies.



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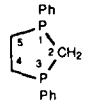

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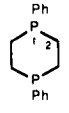

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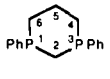

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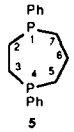

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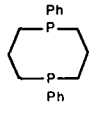

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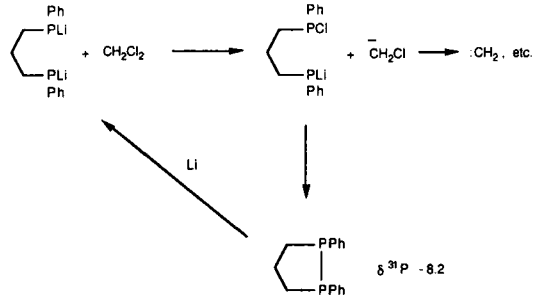
† Author to whom all correspondence should be addressed.

When we began this work few cyclic diphosphines were known and their stereochemistry was uninvestigated. Thus, Hinton and Mann[4] obtained **3** from dibenzylphenylphosphine by sequential quaternisation with 1,2-dibromoethane and reduction with lithium aluminium hydride to remove benzyl and, by an extension of this method to tribenzylphosphine, 1,4-diphospha (2,2,2) bicyclooctane was obtained in very low yield. Subsequently, Issleib and his collaborators[5–7] obtained **2** and **3** from the diphosphide **1** ($n = 2$) and the appropriate dihalide. The P-ethyl and P-cyclohexyl analogues of **3** were prepared similarly. Though well characterised, no indication of stereochemistry was given by either group though Issleib obtained two disulphides from both **3** and its P-cyclohexyl analogue. After the work to be described here was finished a paper appeared[8] describing the preparation of **2, 4** and **1** and the separation of stereoisomers of **4** via their platinum complexes. We discuss these results below together with our own.

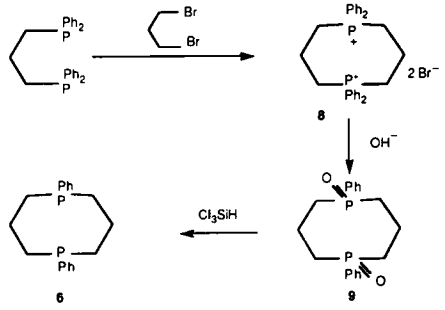
RESULTS

The heterocycles **2** and **3** were prepared from the diphosphide **1** ($n = 2$) and **4** and **5** from **1** ($n = 3$) by reaction with the appropriate dichloroalkane. Yields are variable, the major byproduct being polymer which is often difficult to separate. In the preparation of **4** intramolecular cyclisation was the major pathway, presumably proceeding as shown (Scheme 1).



SCHEME 1

It was identified by its ^{31}P chemical shift and by its conversion to the starting diphosphide on treatment with lithium. This reaction apart, the factors affecting cyclisation versus polymerization are not clear. In agreement with Issleib's observations[5] we noted that addition of the phosphides to the dihalides gave better yields than the reverse procedure. Also, in general, use of diethyl ether as a solvent for the dihalide gave better yields than tetrahydrofuran alone. Carrying out the reactions at high dilution did not appear to improve yields. The highest conversion (as indicated by ^{31}P n.m.r.) was for the 1,4-diphosphepane, **5**. The 1,5-diphosphocane **6** was prepared by the more circuitous route shown (Scheme 2). This sequence has the practical advantage of utilising air-stable materials till the last step. Surprisingly, only one of the isomeric dioxides, probably *trans* **9**, appears to reduce to the phosphine with Cl_3SiH. We observed (^{31}P nmr) only



SCHEME 2

unchanged phosphine oxide in the attempted reduction of *cis*-2 but this may be due to much more rapid oxidation of the *cis* isomer during workup. The direct preparation of **6** from **1** ($n = 3$) and 1,3-dibromopropane afforded a product with markedly different ^{31}P n.m.r. but we have been unable to separate this from accompanying polymer. The worst yields (5–10%) were obtained for **4** and the alternative method[8] utilising the diphosphide **1**, (R = Li, $n = 1$) prepared by a lengthier route (it cannot be obtained by the cleavage reaction) is clearly preferable (yield 41%). However, this method did not give solid products for **2** and **4**. The preparations are summarised in Table I.

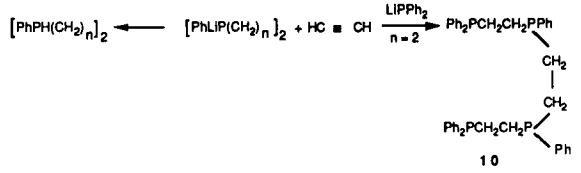
We briefly explored an alternative approach to the heterocycles utilising Aguiar's observation[9] that lithium diphenylphosphide adds to acetylene to give **1** ($n = 2$, R = Ph). However the favoured reaction with the diphosphides (**1** R = Li, $n = 2$–5) is deprotonation of the alkyne, though we could observe (by ^{31}P n.m.r.) low yields of cyclic diphosphines when the reaction was carried out in the presence of a strong organic base. Interestingly when acetylene was passed into a

TABLE I

Properties of heterocycles **2–7**

Compound	mp (°C)	δ ^{31}Pa	Found %C	Found %H	Calculated %C	Calculated %H
2 *cis*	51–52	−0.75[b]	69.6	6.15		
					69.6	6.25
2 *trans*	76–77	−1.5[b]	69.5	6.11		
3 *cis*	98–101	−27.5	70.1	6.9		
					70.6	6.7
3 *trans*	168–170	−28.0	70.5	6.9		
4 *cis*	[c]	−34.1[b,c]				
4 *trans*	53–54°	−33.3[b]	70.5	6.5	70.6	6.7
5 *cis*	72–73	−20.3	71.1	7.0		
					71.3	7.0
5 *trans*	73–74	−25.9	70.1	7.1		
6 *cis*	—	−29.1[c]	—		—	
6 *trans*	74–76.5	−21.1[d]	69.75	7.4	69.9	7.4
7	—	−27.6[b]	—		—	

[a] In ppm from external $(DO)_4P^+$; upfield shifts are negative.
[b] H. Schmidbaur, S. Schnatterer, *Chem. Ber.*, *1986*, **119**, 2832; δ ^{31}P: **2**, −0.75, −1.5; **4**, −33.3, −34.5.
[c] Not isolated; value obtained from thermal isomerisation mixture.
[d] Obtained as a hemihydrate.



SCHEME 3

solution containing both the diphosphide **1** ($n = 2$) and lithium diphenylphosphide, a good yield of the known[10] tetraphosphine, **10**, was obtained. This presumably reflects the lower basicity of Ph_2PLi, allowing it to add to acetylene to give vinyldiphenyl phosphine which is less acidic than acetylene but still susceptible to Michael addition by the powerfully nucleophilic diphosphides.

The proton source in this reaction is acetylene as indicated by the brisk evolution of gas when the reaction mixture is quenched with water. Potentially, this reaction could be applied to the preparation of other tetraphosphines and may be useful as the preparation of secondary phosphines could be avoided.

SPECTRA AND STEREOCHEMISTRY

The solid state structure of **3** was established by x-ray crystallography of the *trans*-isomer[11] (Figure 1); characteristically, the phenyl groups are diaxial. Unfortunately we were unable to obtain suitable crystals of the *cis* form as it would have been interesting to know if this diaxial preference would force the ring into a boat conformation as has been observed for other phosphorus heterocycles[12a]. As expected, oxidation with hydrogen peroxide converts the two isomers stereospecifically into the corresponding dioxides whose stereochemistries have also been established by x-ray studies.[15] Treatment of the *cis*-isomer with sulphur affords a disulphide, m.p. 255–258°, agreeing with the higher melting of the two disulphides previously reported by Issleib and Standtke (m.p. 253°). The lower melting isomer (m.p. 154°) obtained by these workers is therefore the *trans* **3** disulphide. Apart from **3**, stereochemical assignments have been based on spectra and to that extent are tentative.

^{31}P NMR

This is of little direct stereochemical value and we have found no consistency in δ values for *trans* versus *cis*. In theory it should be possible to assign stereochemistry from the low temperature ^{31}P data since, when conformational flipping is frozen either by low temperature or in the solid state, the δ values for the two phosphorus nuclei in any one stereoisomer are not necessarily the same. Thus, in the case of **3** the *cis*-isomer will have a phosphorus with an axial phenyl and one with an equatorial phenyl (assuming chair forms); hence the ^{31}P spectrum should be an AB quartet. Instrumental difficulties prevented us from exploring this unambiguous route and at the lowest temperature we could reach ($\sim -30°$) we observed no more than line-broadening for *cis*-**3** though *trans*-**3** showed no signs

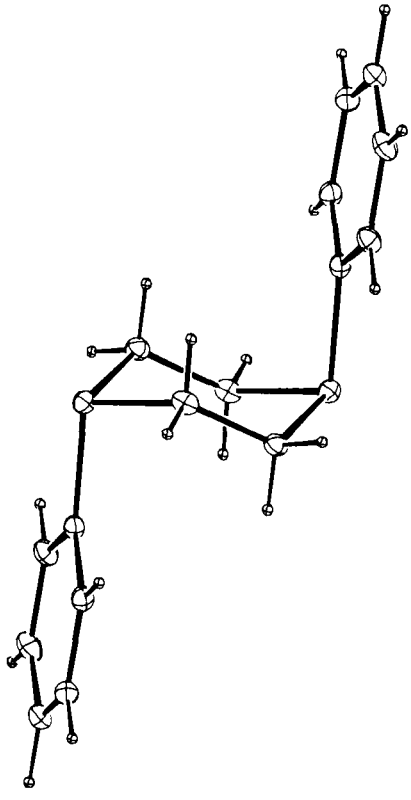


FIGURE 1 Computer drawing of solid state structure of *trans*-**3**. The molecule is centrosymmetric. Some representative bond lengths and bond angles are: P–C aliphatic 1.838(3), 1.849(3), P–C aromatic 1.832(3); endocyclic CP̂C 100.1°, exocyclic CP̂C 102.7(1), 102.4(1), endocyclic PĈC 117.9(2), 117.7(2) torsional PCCP 59.8°(3).

of change. However Schmidbaur and Schnatterer[8] observed an AB pattern at −92° for one of the isomers of **4** which is thus the *trans*-isomer since the phosphorus atoms are in a 1,3-relationship. Comparison of ^{31}P chemical shifts confirms that our single isomer of **4** is also *trans*. The same workers observed no change at −60° in the spectra of **2** or **7**. It follows from these studies that conformational flipping is rapid at room temperature, a barrier of only 36 kJ mol^{-1} having been found for *trans* **4**. Stereochemistry apart, the ^{31}P spectra show no anomalies; notable is the sharp downfield shift in the five-membered ring, reflecting similar behaviour in other organophosphorus compounds[12a].

^{1}H SPECTRA

The ^{1}H and ^{13}C spectra of the heterocycles show strong second order effects due to the symmetry of the molecules and, for ^{13}C, to the presence of more than one coupling pathway between the same nuclei. Nevertheless, it would be expected that the ^{1}H spectra of the PCH_2P fragment of **2** would be markedly different in

the two stereoisomers, specifically the high symmetry of the *trans*-forms should make the chemical shift of each proton of the 2-methylene identical whereas in the *cis*-forms it should be possible to distinguish two different protons. Similarly, the cis-isomer of **4** should be locked in the conformer with the two phenyl groups equatorial in order to avoid what would otherwise be a very severe 1,3-diaxial interaction, giving rise again to two non-identical protons in the PCH_2P grouping. Though conformational effects are expected to be less pronounced in rings containing phosphorus, presumably because of the greater length of the phosphorus-carbon ring bonds and the known axial preference of substituents at ring phosphorus, it would be surprising if they were not dominant in **4**. Since there is a strong angular relationship betweenthe coupling constant and the orientation of the lone pair on phosphorus and the adjacent protons, a considerable difference between the ^1H spectra of the PCH_2P fragment for the diastereoisomers of both **2** and **4** is expected[13a].

In the event the lower-melting of the two isomers of **2** shows a 1 proton multiplet as an apparent doublet of triplets (δ 2.54, J14.9, 25.3 Hz) to low field of a five proton, very complex, multiplet (δ 2.21). The other isomer however has three two proton multiplets of which the one to lowest field (δ 2.33, J, 15.7, 18.7) comprises six-lines. Since a larger J value is expected for a *cis* lone pair-proton geometry, δ and J values both indicate that the low melting isomer of **2** is the *cis*-isomer.

The case of **4** is less clear-cut since we were only able to obtain the ^1H spectrum of the *trans*-isomer, which we would expect to be a rapidly interconverting mixture of conformers. The spectrum, though very complex, shows no downfield, one proton, multiplet and hence is compatible with the conclusions drawn from ^{31}P nmr data.[8] The ^1H spectra of **3**, **5** and **6** were extremely complex and afforded no stereochemical information. In an effort to overcome the difficulties of interpretation of the ^1H spectra we prepared derivatives in which one of the phosphorus atoms was converted to its oxide, sulphide or phosphonium salt, in the hope that the removal of symmetry would make the spectra more amenable to interpretation, but the complexity remained even at 500 MHz.

^{13}C SPECTRA

The ^{13}C spectra of the heterocycles (Table II) show marked differences between isomers in both chemical shifts and phosphorus-carbon coupling constants. The spectra are deceptively simple but in fact exhibit strong second order effects making them of little value in assigning stereochemistry. Apparent J values represent the sum of a number of couplings and the magnitudes and signs of these are difficult to estimate because of a paucity of data and the availability of more than one coupling pathway. An example of this is **2** where each of the C_2H_4 carbons is coupled to a phosphorus by one, two and three bond paths. The C_2H_4 carbons appear as complex multiplets (Figure 2) and there is a marked difference between diastereoisomers in the value of the apparent coupling constant (*cis* 10.3, *trans* 19.1 Hz). Though there is a reasonably well established correlation between the proximity of the lone pair to the β-carbon and $^2J_{PC}$[13a], it is doubtful if this

TABLE II

^{13}C spectra of 2–5[a,b]

Heterocycle	C_2	C_3	C_4	C_5	C_6	C_7	J_{PC} values (Hz)
2 *cis*	23.34t		27.75t	27.75t			C2:27.8, C4, 5:10.3
2 *trans*	23.22t		28.87t	28.87t			C2:27.8, C4, 5:19.1
3 *cis*	19.81dd	19.81dd		19.81dd	19.81dd		^2J 4.4, ^1J 10.3
3 *trans*	16.38dd	16.38dd		16.38dd	16.38dd		^2J 4.4, ^1J 19.0
4 *trans*	26.56t		27.67t	22.87t	27.67t		C2:19.0; C4, 6:4.5[d]; C5:8.8[d]
5 *cis*	29.49t	29.49t		29.49t	24.10t	29.49[t]	C2, 3, 5, 7:5.9; C6:13.2
5 *trans*	29.54t[c]	29.54t[c]		29.43t[c]	22.64t	29.43[c]	C2, 3:14.6; C5, 7:14.6; C6:16.85

[a] In ppm from Tms = O; $CDCl_3$ solvent; d = doublet, t = triplet.

[b] cf. acyclic analogues: $Ph_2PCH_2PPh_2$ (δ 27.87, J 23.3) $Ph_2P(CH_2)_2PPh_2$ (δ 23.8; $J < 1$) $Ph_2P(CH_2)_3PPh_2$ (α: δ 29.45, J 12; β: δ 22.2 J 16.5).

[c] These two (δ) values are interchangeable.

[d] The different values reported[8] are due to a transcription error (H. Schmidbaur, personal communication).

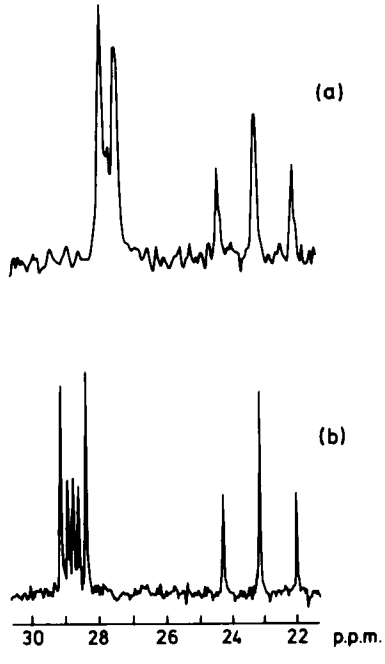


FIGURE 2 The ^{13}C spectra of the aliphatic regions of (a) *cis* **2** and (b) *trans* **2**.

effect is contributing to stereoisomer differences since models indicate that the distance between the lone pair and the β-carbon is roughly the same in both diastereoisomers. The apparent coupling is the sum of $^1J_{PC}$, $^2J_{PCC}$ and $^3J_{PCPC}$ and any simple analysis could be very misleading. The chemical shifts of the ethylene bridges of **2** are well downfield of the acyclic analogue **1** ($n = 2$, R = Ph; $\Delta\ \delta$ *ca.* 4–5 ppm) but almost identical with the value for **1**-phenylphospholan.[14] On the other hand the methylene bridge is upfield of **1** ($n = 1$, R = Ph; $\Delta\ \delta$ *ca.* 4–5 ppm), possibly a substituent effect.

The phosphorinanes **3** and **4** give carbon spectra whose chemical shifts are understandable in terms of known effects.[13b] Most dramatic is the strong upfield shift of the aliphatic carbons of **3** (compared with the α-carbons of 1-phenylphosphorinane[14]) due to shielding by the axial phenyls. This is particularly pronounced for *trans*-**3** ($\Delta\ \delta$-8.4 ppm) and suggests strongly that the solid state conformation persists to a large extent in solution. *Cis*-**3** aliphatic carbons absorb appreciably downfield of those in the *trans*-**3** ($\Delta\ \delta$3.4 ppm) presumably reflecting the fact that only one phenyl can be axial in either chair conformer and that conformer interconversion is rapid. The corresponding dioxides of **3** show a similar correlation of solid-state-solution conformations. In the solid state the oxygens are axial in *trans*-**3** dioxide[15] and in solution the ring carbons of this isomer (δ 24.1) absorb at lower field than the *cis* (δ 22.9), a result compatible with a conformer population favouring equatorial phenyls. The bisbenzylbromide salts of **3**, however, show negligible difference in the δ values for the ring aliphatic carbons of the two isomers (13.65, 13.67) reflecting the very similar steric environment with two bulky groups on each phosphorus. The *trans* 1,3-diphosphorinane, **4**, must have one phenyl axial and this will shield C_5 in either conformer making this the most upfield carbon. The *trans* isomer isolated by us shows a carbon to higher field than any in 1-phenylphosphorinane. Unfortunately we were unable to compare this with the *cis*-isomer in which no such effect should be apparent as the conformation should be locked with both phenyls equatorial. The ^{13}C data for *cis*-**4** obtained by Schmidbaur and Schnatterer[8] rather surprisingly show C_2, C_4 and C_5 upfield of the corresponding carbons in the *trans*-isomer. The splitting pattern for the ring carbons of both isomers of **3** has the appearence of a first order doublet of doublets. The corresponding dioxides, while also showing a four line pattern (*cis*, δ 22.93, J 70.5, 8.4, *trans*, δ 24.13, J 71.7, 10.1) have the appearance of AB quartets. The bis benzylbromide salts, on the other hand, show more pronounced second order effects and somewhat greater isomer differences in $^1J_{PC}$ (J: *cis*, 9.5, 44.05; *trans*, 9.05, 53.55). A simple pattern, a triplet of triplets (approximate ratio 1:1:2), is observed for *trans*-**4** and the inherently complex nature of these spectra is further exemplified in the diphosphepane **5** whose ^{13}C spectrum consists of a pair of triplets in an approximate ratio of 1:4. The aromatic carbons of all the diphosphorus heterocycles examined show the α-carbons usually as a broad singlet at δ 137–140 except for **2** which showed a doublet ($J = 18$ Hz) in both isomers. The o-carbons were pseudo-triplets (δ 130.4–131.7; $J = 8.0$–14.6 Hz). There were no or only weak apparent second order effects on the meta doublets (δ 128.1–128.65; $J = 2.5$–5.9 Hz) or para singlets (δ 127.5–128.7). These chemical shift values are unexceptional and differ little from those for other aryl phosphines.[14,16]

INFRA-RED SPECTRA

Unexpectedly, the isomer pairs show useful differences in their infrared spectra in the 700–850 cm^{-1} region associated with C–H out of plane deformation and out-of-plane skeletal mode absorptions for monosubstituted aromatics. The bands in this region of *trans*-**3** are doubled in *cis*-3 (Fig. 3) and similar behaviour is observed in **2**. Similarly one of the isomers of **5** shows twice as many bands in this region as the other. However, we think the isomer of **5** showing the doubling is the *trans* rather than the *cis*-isomer on other grounds. Also, *trans*-**4** shows this splitting, so it would be unwise to make any correlation without more data. The single isomer of **6** which we obtained shows two weak and two strong peaks in this region. The data are summarised in Table III. Behaviour of this type has been observed, though rarely, in some aryl-substituted alkene stereoisomers,[17] though its origins are unknown. No such differences are seen in the spectra of the corresponding isomeric dioxides or phosphonium salts of **3**.

MASS SPECTRA

All the heterocycles isolated showed the appropriate molecular ions in their EI mass spectra. In addition they all showed peaks at m/z 185 and 183 shown by

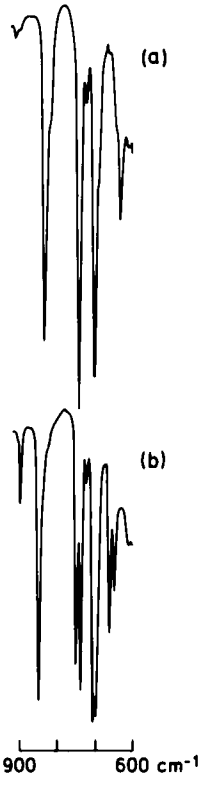


FIGURE 3 The infrared spectra of (a) *trans* **3** and (b) *cis* **3**.

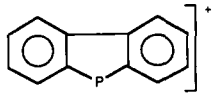
TABLE III

Infrared spectral data for 2–6[a]

Heterocycle	*cis*	*trans*
2	850	838
	751, 739	745
	707, 699	705
3	809,	800
	753, 739,	733
	705, 720	700
4	—	808[b]
		753, 765,
		712, 727
5	700	702, 722
	750	747, 807
6	762[b], 750	
	737[b], 702	

[a] In cm^{-1} in paraffin mulls. All bands are medium to strong unless noted.
[b] Weak.

Williams and his collaborators to be characteristic of $[Ph_2P]^+$ and the phosphafluorenium ion **11** respectively.[18] Formation of these ions in our heterocycles must be preceded by phenyl migration, presumably intramolecular, from one phosphorus to another.



11

Phenyl migration from phosphorus to phosphorus has been observed in the $Ph_2P(CH_2)_nPPh_2$ ($n = 1,2$) and analogous diarsines[19] and the effect appears independent of chain length since we have observed similar behaviour in $Ph_2P(CH_2)_nPPh_2$ ($n = 3$–6).[20] Assuming that the phenyl transfer is intramolecular, it might be expected that the process would proceed best in the *trans* isomer of the heterocycles and we did indeed observe m/z (183 + 185) to be more intense in the *trans* forms than in the *cis*. However, we have no knowledge of the sequence of fragmentations and particularly as **2**, **3** and **5** showed strong peaks corresponding to loss of C_2H_4 from the parent, a much more detailed study of the fragmentation patterns would be required before drawing conclusions from simple observation of peak intensities was justifiable. Nevertheless, the fact that these observations agree with our assignments by other methods suggests that such a correlation might be a useful one. The dioxides of **2** and **3** also show analogous peaks corresponding to phenyl migration (m/z 199, 201, Ph_2PO^+). Apart from the observed rearrangement the mass spectra of **2**–**6** show no unusual features.

THERMAL EQUILIBRATION STEREOISOMERS

We have examined the thermal *cis* ⇋ *trans* interconversion of the stereoisomers of **2–5** to see if any obvious ring effects were operative. The results are summarised in Table IV. Kinetic data were obtained for **2** and **3** from ^{31}P spectra, and utilising standard relationships,[21] values of $\Delta G\ddagger$ 156.7–163.7 kJ mol^{-1} were calculated. This suggests that the barrier to inversion differs little from monophosphorus 5- or 6-membered[22,23] (147–150 kJ mol^{-1}) or, indeed, acyclic phosphines.[23,25] Slightly higher values in the diphosphorus heterocycles are probably of little significance since, as Berlin and his collaborators have observed,[23] some oxidation invariably occurs after prolonged heating and the presence of these oxidation products may well affect rate measurements. This is reflected in the fact that good linear plots were not always obtained. Nevertheless, all equilibria were approached from both directions and, in the case of **2** and **3**, starting from single stereoisomers.

It is obvious that there is not a large energy difference between stereoisomers in **3–5**; the difference observed for **2** presumably reflecting the more crowded nature of the smaller ring. Most unusual is the rapid isomerisation of **5**. However, this result is based on a single observation and will need to be repeated for confirmation. Preparation of **5** gave initially only a single isomer (by ^{31}P n.m.r.) which appeared to undergo some isomerisation during isolation ($T \leq 90°$). There seems no reason for a dramatically lowered inversion barrier and it is possible that some impurity catalysis is operating. The equilibrium mixture of **5** is predominantly the non-kinetic isomer and we suggest that the thermodynamically more stable of the isomers is *trans*. Insufficient **6** was obtained for inversion experiments (Table IV).

TABLE IV

Thermal equilibrium data for **2–5** at 413°K[a]

	K_{eq} (t/c)	$t_{1/2}$ (*h*)	$k \times 10^5$	$\Delta G\ddagger$ (kJ mol^{-1})
2 *cis*	6.14	6.6	2.91	156.7
2 *trans*		42.3	0.42	163.7
3 *trans*	0.87	14.9	1.29	157.5
4 *trans*	1.5	18[b]	—	—
5	1.86	*ca.* 0.5[b]	—	—

[a] Solvent dimethyl formamide.
[b] Time to reach equilibrium beginning with a single isomer.

EXPERIMENTAL

General: All compounds were colourless except for the phosphides. All operations were performed under argon and solvents (dried and distilled) were deoxygenated by saturating them with the inert gas. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ immediately before use. The diphosphines, $Ph_2P(CH_2)_nPPh_2$, were commercial materials (Strem. Chemicals) with correct m.pts. and free of impurities by ^{31}P n.m.r. The diahlides, $X(CH_2)_nX$ (X = Cl, Br), were commercial products purified by simple distillation. The dioxides and bis benzylquaternary salts of **3** were obtained as previously described.[27] Infrared spectra were measured as paraffin mulls and nmr were taken in $CDCl_3$ or $CHCl_3$

unless otherwise noted. Instrumentation was described in previous papers and microanalyses were performed by Dr. P. Pham of this School.

Preparation of diphosphines **2–5**. *General Procedure*: To a stirred solution of the appropriate dihalide (*ca.* 0.1 M in ether) was added dropwise via canula a solution (*ca.* 0.1 M in THF) of the required diphosphide, **1**[3]. The product mixture was isolated either by evaporation followed by benzene extraction of the residue or (better) by quenching with water & $CHCl_3$ extraction. When the diphosphide **1** ($n = 2$, R = Li) was used better yields were obtained by using recrystallized diphosphide as this ensured the absence of $LiPPh_2$. If this is not done the heterocycles may be separated best from acyclic material by extraction into 2.5 MHCl followed by basification and re-extraction.

Of the crude diphosphines isolated as above only **5** could be recrystallised directly (ether) and was isolated in 64% yield. The other heterocycles were freed of polymer and separated into stereoisomers by chromatography over silica gel and elution with toluene-cyclohexane mixtures (usually *ca.* 1:1). Consequently the yields of isolated materials were poor (5–30%) and varied somewhat from preparation to preparation. The reactions were monitored by ^{31}P nmr. The ratio of stereoisomers initially formed was unrelated to the equilibrium mixtue. In the case of **5** only the *cis* isomer was formed and the *trans* isomer was obtained by chromatographic separation of the mixture obtained by thermal equilibration of the kinetic product. Physical constants, analytical and spectral data are given in Tables I–III.

With the exception of **2** (see text), ^1H spectra are of little value, the ring protons invariably appearing as complex unresolved multiplets: **3**, δ 2.25, **4** δ 1.6, 2.1, 2.4; **5** ~ δ 1.9, 2.3, 2.55. Integrals agreed with the expected structures.

cis-1,4-Diphenyl-1,4-diphosphorinane disulphide. *Cis*-**3** (69 mg) and S_8 (15.5 mg, 0.95 mol) were warmed gently in benzene, the solution evaporated to dryness taken up in $CHCl_3$ and stored at *ca.* −6° overnight. The crystals which separated were the *disulphide*, m.p. 255–258°. Found: C, 57.2; H, 5.6, S 19.4; *m/z*, 336. $C_{16}H_{18}P_2S_2$ requires: C, 56.95, H, 5.4; S, 19.05; M.W. 336. ν_{max} 710 s, 620 m cm^{-1} (P═S), δ ^{31}P 33.3.

1,5-Diphenyl-1,5-diphosphocane **6**. Propane-1,3-diylbisdiphenylphosphine (8 g) in dimethyl formamide (DMF, 150 ml) and 1,3-dibromopropane (4 g; 1.1 mol) in DMF (150 ml) were placed in separate dropping funnels fitted to a 1 l three-necked flask fitted with a condenser and containing DMF (250 ml) and a magnetic stirrer bar. The solvent in the flask was stirred and refluxed and the two reactants added dropwise and simultaneously during 2.5 h and refluxing continued for a further hour. The solvent was distilled off and the residue recrystallised twice from ethanol giving 1,1,5,5-tetrapheny-1,5-diphosphocanium dibromide, **8** (2.65 g, 28%) essentially pure, m.pt, 330–333°, as the trihydrate. Found: 53.55; H, 5.25. $C_{30}H_{32}Br_2P_2$ $3H_2O$ requires: C 53.6; H, 6.25 δ ^{31}P 25.4' ^1H nmr (CD_3OD): δ 2.43, tt, *J* 23.0, 4.6 Hz, 4.5 H ($CH_2\mathbf{CH_2}CH_2$), 3.90 cm, 8 H (PCH_2), 7.9 cm 24 H (ArH). Both ethanol and water were present (^1H nmr, ir). The salt **8** (2.6 g) was added to KOH (6 g) in H_2O (55 ml) and the mixture stirred and heated on the steam bath till no salt remained by TLC. The solution was extracted twice ($CHCl_3$), and the organic layer dried and evaporated to give a mixture of *cis*- and *trans*-1,5-diphenyl-1,5-diphosphocane-P,P-dioxides in roughly equal amounts (^{31}P nmr) (1.2 g, 85%) m.pt. 189–192°. Found C, 60.0, H, 6.6, *m/z* 332 $C_{18}H_{22}O_2P_2$ 1.5 H_2O requires: C, 60.2; H, 6.7%, M.W. (anhydrous) 332. ν_{max} 3470, 1600 (H_2O), 1170 s (P═O) cm^{-1}. ^1H nmr: δ 2.5 cm 12 H (CH_2); 7.65 cm 9 H (ArH). The dioxides were separated by chromatography over silica gel (chromatotron) and elution with CH_2Cl_2–Pr'OH(4:1) to give isomer A, m. pt. 229–231°, δ ^{31}P 40.4; *m/z* 332. Further elution with CH_2Cl_2:MeOH (1:1) afforded isomer B, m. pt. 209–211°, δ ^{31}P 39.1; *m/z* 332. We tentatively assign *trans* geometry to isomer A because of its higher melting point.[27] Isomer A (200 mg) was dissolved in a solution of $HSiCl_3$ in benzene (2.3 M, 5 ml) and the mixture stirred and refluxed (2 h) till TLC showed only traces of starting material. The cooled reaction mixture was washed with an equal volume of aqueous NaOH (40%) and the dried organic layer evaporated to give crude, presumably *trans, diphosphine*, **6** (120 mg), 65%). No oxides could be detected (^{31}P nmr). Recrystallisation (EtOH) gave long needles, m. pt., 74–76.5°. Found: C, 69.75; H, 7.4 *m/z* 300. $C_{18}H_{22}P_2$ 0.5 H_2O requires: C, 69.3; H, 8.1% M.W. (solvent free) 300. ν_{max} 3350, 1590 (H_2O). δ ^{31}P-21.1. Attempted reduction of isomer B resulted only in recovery of starting material.

Thermal Isomerisations. Samples of pure isomers or mixtures containing very largely one isomer, were dissolved in deoxygenated DMF in 10 mm nmr tubes fitted with a serum cap and flushed with argon. The tubes were immersed in an oil bath maintained at 140° and removed periodically, cooled rapidly, and the $\{^1H\}^{31}P$ nmr determined. The mean of three integrals was taken and the results plotted in the normal way. Where necessary, corrections were made for the different responses of the

different isomers by measuring the integrals for mixtures of known amounts since rather surprisingly, the NOEs of different stereoisomers are not the same. At least two runs were carried out for each of **2**, **3** and **4**. Experiments run in *o*-dichlorobenzene showed no substantial differences.

ACKNOWLEDGEMENTS

This work was supported by the Australian Research Grants Scheme; one of us (MB) thanks the School of Chemistry for the award of a summer scholarship.

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