Bicyclic Phosphanes: Synthesis, Stereochemistry, and Conformation

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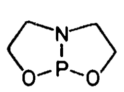
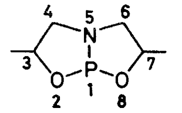
From the new family of 2,8-dioxa-5-aza-1-phospha^{III}bicyclo[3.3.0]octanes (bicyclic phosphanes) (1)—(5), three derivatives (3)—(5) were studied by synthesis, oligomerization, and n.m.r. spectroscopy. Conformational analysis shows that the five-membered rings take on an envelope conformation. The orientation of the folds is known for the majority of the compounds. Comparison of stereochemical data between phosphanes (2)—(4) and the corresponding 1-phenyl-2,8-dioxa-5-aza-1-phospha^{V}bicyclo[3.3.0]octanes (bicyclic phosphoranes) (7a)—(9a) underlines the conformational consequences due to the change of hybridization of the nitrogen and phosphorus atoms.

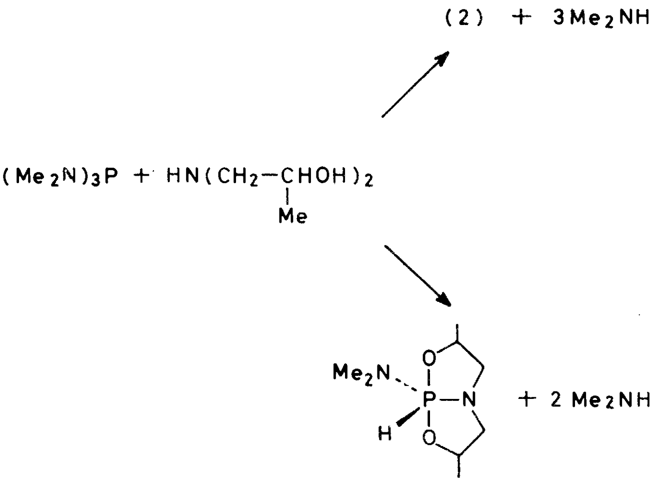
In a note published in 1977,[1] we described the bicyclic 2,8-dioxa-5-aza-1-phospha^{III}bicyclo[3.3.0]octanes (phosphanes) (1) and (2). Although structurally quite simple, they were, to our knowledge, the first phosphorus derivatives of this kind ever described; however the arsenic homologue of (1) has been known since 1970.[2] Such compounds were not obtained sooner due to two difficulties we met during our first approach. (i) First, the compounds tend to oligomerize quite easily. For phosphane (1) oligomerization is so fast that we could not isolate the monomer. For (2) the presence of substituents slows down this phenomenon; we were able to obtain (2) in its monomeric form but in meagre yield. (ii) The second difficulty comes from the fact that these compounds can add any molecule with a mobile hydrogen. Thus the attempted preparation of (2) by the action of tris(dimethylamino)phosphane, $(Me_2N)_3P$, on the corresponding 3-azapentane-1,5-diol leads to the formation of phosphorane (7b) with a P–H bond. The diminution of the amount of this phosphorane requires heating at 140 °C during 10—15 h. We propose Scheme 1 for this reaction. Two routes could lead to phosphorane (7b): (a) intermolecular oxidative addition of the dimethylamine to the bicyclic phosphane, and (b) intramolecular oxidative addition of the N–H group in the tautomeric form $(7b)_{open}$, which is formed during the synthesis.



(1)

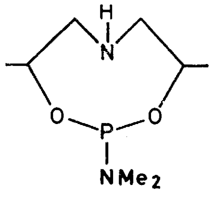


(2)



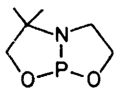
(7b)

Scheme 1

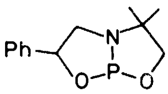


(7b) open

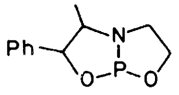
These two observations show that double cyclisation confers on the bicyclic phosphanes particular properties not met with in the corresponding acyclic amino(dialkoxy)phosphanes $R_2NP(OR)_2$. We were thus prompted to continue our research in this field. This paper describes the three new bicyclic phosphanes (3)—(5)



(3)

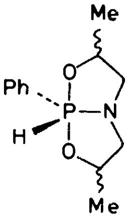


(4)

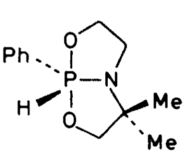


(5)

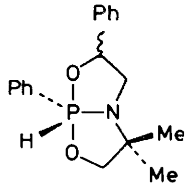
which derive from asymmetric 3-azapentane-1,5-diols, including their synthesis, stereochemistry, and conformation. The conformational study also includes compound (2) as well as a comparison with the bicyclic phosphoranes (7a)—(9a) formed from the same aminodiols.



(7a)



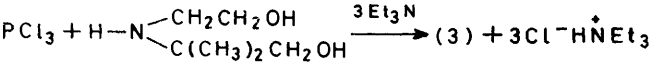
(8a)



(9a)

RESULTS AND DISCUSSION

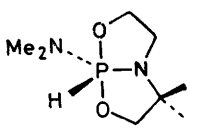
Synthesis.—Simple in its principle, the corresponding aminodiol acting either on tris(dimethyl amino)phosphane (Scheme 1) or on phosphorus trichloride in the presence of a base (Scheme 2), the synthesis is rather delicate owing to the secondary products which are formed. Thus in the preparation of phosphane (3) from $(Me_2N)_3P$, the analysis of the ^{31}P n.m.r. spectrum of the crude product shows five peaks, four singlets and a doublet, in the approximate ratio 50 : 20 : 5 : 10 : 15.



$$PCl_3 + H-N\begin{array}{l}\diagup CH_2CH_2OH\\ \diagdown C(CH_3)_2CH_2OH\end{array} \xrightarrow{3Et_3N} (3) + 3Cl^-\overset{+}{H}NEt_3$$

SCHEME 2

The major peak, at δ 147.7 p.p.m. belongs to (3), obtained in pure form by distillation and whose monomeric character was established by ^1H n.m.r. The doublet, centred at δ —41.4 p.p.m. with a ^1J(P–H) of 820 Hz is attributed to the phosphorane (8b) and this was checked by the interaction of dimethylamine with pure (3). The signals at δ 130.5, 139.1, and 144.8 p.p.m. probably belong to oligomeric species. In the spectrum of the crude product obtained from PCl_3, the doublet belonging to (8b) is absent, and the four signals at weaker field are found with slightly different relative intensities indicating a decrease in the proportion of (3). The spectrum of the distilled fraction shows a single signal at δ 147.7 p.p.m.



(8b)

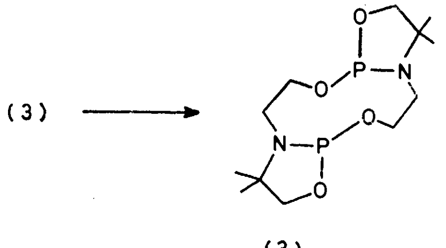
The synthesis of phosphanes (4) and (5) follows a similar course with the difference that the number and intensity of the additional ^{31}P signals assigned to the oligomeric species are noticeably weaker.

Oligomerization.—The marked tendency of bicyclophosphanes towards oligomerization is one of the main obstacles to their purification. This explains, to an extent, why such low yields are obtained in these reactions. We shall exemplify this statement by describing the rather different behaviours of compounds (1) and (3).

For phosphane (1) when $HN(CH_2CH_2OH)_2$ reacts with $(Me_2N)_3P$, the ^{31}P n.m.r. spectrum of the mixture shows two signals at δ 139 and 134 p.p.m. assigned to monomer and oligomers, respectively. At the end of the reaction, the ratio of these two species is *ca.* 60 : 40 and it changes inceasingly until it becomes constant at 15 : 85 after 15 days. This modification is accompanied by a progressive thickening of the mixture which ends as a whitish solid insoluble in the toluene used as solvent. The mass spectrum of the crude sample recorded 48 h after the end of the reaction reveals the presence of species with a molecular weight greater than 1 000. All attempts at isolating a pure product failed.

In contrast phosphane (3) was isolated as a pure monomer. Freshly distilled, it is a mobile liquid. The ^1H n.m.r. spectrum of the benzene solution, which shall be analysed in detail, is characteristic of a pure product. There are two singlets at δ 0.76 and 1.01 which can be assigned to the diastereotopic CH_3 groups. At room temperature this liquid becomes a solid after a week. The ^{31}P n.m.r. spectrum of a benzene solution of this solid shows two additional peaks at δ 146.0 and 149.7 p.p.m. The species corresponding to the last signal separates from the solution as a solid; its solubility in benzene is rather low and its ^1H n.m.r. spectrum is quite different from that of the pure monomer. In particular the CH_3 groups give two singlets at δ 0.80 and 0.95. Mass spectrometry (ionization by electron impact or by field desorption) clearly shows that this species is a dimer of (3).

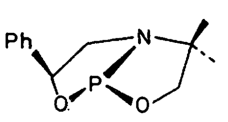
By analogy with the results of Albrand and his co-workers [3] and Dutasta and his co-workers,[4] who have shown that dimerization takes place in five-, six-, and seven-membered phosphorus rings, we can propose the structure $(3)_{\text{dim}}$. for the dimer of phosphane (3). This process leads to a ten-membered ring derivative which takes into account the higher stability of the substituted ring on one hand, and the equivalence of the CH_3 groups on the other. (In the ^1H n.m.r. spectrum, only two singlets correspond to the four CH_3 groups). An *X*-ray study has been undertaken to establish the structure of this dimer.



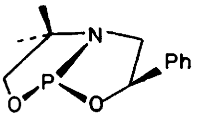
$(3)_{\text{dim}}$

Stereochemistry.—The asymmetry of the aminodiols used in the synthesis produces a chiral phosphorus atom in phosphanes (3)—(5). In the case of (4) and (5), this chirality is added to that of one or two carbon atoms; this leads to an interesting problem of stereochemistry.

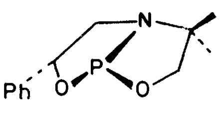
Neglecting the highly constrained configuration in



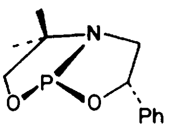
(4′)



($\bar{4}'$)



(4″)

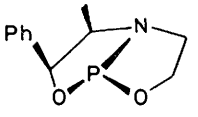


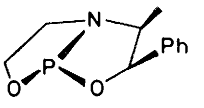
($\bar{4}''$)

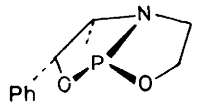
which the lone pairs on phosphorus and nitrogen are *trans*, phosphane (4), formed from racemic 4,4-dimethyl-1-phenyl-3-azapentane-1,5-diol, exists as two racemic diastereoisomeric mixtures $(4') + (\bar{4}')$ and $(4'') + (\bar{4}'')$.

The ^{31}P n.m.r. spectrum of a distilled sample, whose monomeric character was confirmed by mass spectrometry shows two signals at δ′ 152.0 and δ″ 157.4 in the ratio 85 : 15. The analysis of the ^1H n.m.r. spectrum also shows the presence of two species in a ratio roughly equal to that determined from ^{31}P n.m.r. So, two diastereoisomers were obtained as expected although one, probably $(4') + (\bar{4}')$, is predominant.

Phosphane (5) has three chiral atoms, phosphorus and two carbons. The aminodiol used for its preparation is racemic norephedrine, $HOCH(C_6H_5)CH(CH_3)NH_2$. The *RS*/*SR* relationship between the absolute configurations of the carbon atoms reduces the number of the theoretically possible isomers from eight to four. In consequence, as for (4), compound (5) forms two racemic diastereoisomeric mixtures, $(5') + (\bar{5}')$ and $(5'') + (\bar{5}'')$.


(5′)


$(\bar{5}')$


(5″)

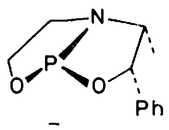
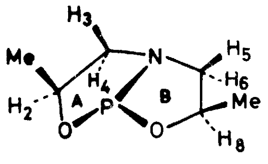

$(\bar{5}'')$

TABLE 1

250 MHz ^1H N.m.r. parameters of phosphanes (2)—(5), solvent C_6D_6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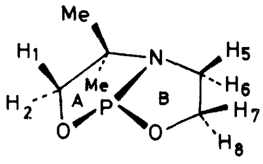
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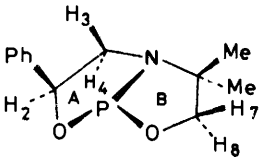
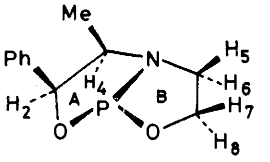

(4)


(5)

	(2) [a]	(3)	(4) [b]	(5)		(2) [a]	(3)	(4) [b]	(5)		(2) [a]	(3)	(4) [b]	(5)
δ(1-H)		3.18			$J_{1,2}$ [c]		−8			$J_{5,6}$	−13	−13		−11.5
δ(2-H)	3.98	2.66_4	4.41_2	4.53_6	$J_{1,3}$					$J_{5,7}$		5.5		6
δ(3-H)	2.72		2.64		$J_{1,4}$					$J_{5,8}$	11	11		11
δ(4-H)	3.14		3.20_8	2.92_3	$J_{1,P}$		14			$J_{5,P}$	0	0		<1
δ(5-H)	2.72	2.36_4		2.72	$J_{2,3}$	11		11		$J_{6,7}$		<1		<1
δ(6-H)	3.14	2.57_8		2.50	$J_{2,4}$	4.5		4.5	5	$J_{6,8}$	4.5	4.5		5.5
δ(7-H)		3.18_4	3.46	3.31_2	$J_{2,P}$	0	<0.8	0	0	$J_{6,P}$	13	13		11.5
δ(8-H)	3.98	2.72_6	3.01_6	3.08_8	$J_{3,4}$	−13		−14		$J_{7,8}$		−8	−8.5	−8
$δ(CH_3)$	1.24	0.672	0.78	0.676	$J_{3,P}$	0		0		$J_{7,P}$		14	15.5	10.5
$δ(CH_3)$		1.00	1.08		$J_{4,P}$	13		15	10	$J_{8,P}$	0	0	<0.3	0

[a] *meso*-Derivative. [b] Main diasteroisomer. [c] Coupling constant in Hz.

The synthesis leads in fact to a single diastereoisomer with one signal at δ′ 141.4 p.p.m. in the ^{31}P n.m.r. spectrum. The ^1H n.m.r. spectrum (which shall be analysed further on) is obviously characteristic of a pure diastereoisomer. We will demonstrate that is is $(5') + (\bar{5}')$.

Conformation.—The construction of a molecular model of the bicyclic phosphane is possible only when tetragonal geometry is attributed to the nitrogen atom and when its lone pair is oriented in a pseudo-π position in relation to that of the tetragonal phosphorus atom (*cis*-junction [5]).* Thus, the skeleton of these molecules appears as a two-pitched roof, the lone pairs of phosphorus and nitrogen being located on the roof.

It was then interesting to carry out a conformational study of the five-membered ring. This study was performed, in the classical way, by detailed analysis of the ^1H n.m.r. parameters listed in Table 1.

Examination of Table 1 shows an important difference between the values of the vicinal coupling constants ^3J(H-C-C-H), 4.5—5.0 Hz for *cis*-coupling and 11.0 or nearly 0 Hz for *trans*-coupling. The same tendency also exists between the coupling constants of the different protons with phosphorus. This clearly indicates that the five-membered rings have a blocked conformation. This is to be expected as the double cyclisation is accompanied by strong constraints.

Examination of molecular models shows that the most likely blocked conformation taken on by the rings is an envelope form, the carbon atoms linked to oxygen atoms being at the end of the folds. These folds can be oriented both *cis* in respect to the lone pairs of phosphorus and nitrogen atoms leading to the *exo*–*exo*-conformation, or both *trans*, giving the *endo*–*endo*-conformation, or in an alternating manner, giving the *exo*–*endo*-conformation.[5] So it is interesting to specify

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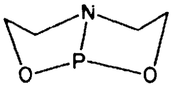
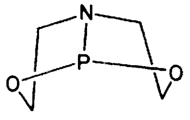
* A photoelectron spectral study of bicyclic phosphanes (1), (2), and (5) has shown that the interaction between phosphorus and nitrogen atoms, usually strong when they are directly linked, is, in this case, very weak.[6] One should expect strong basicity for a nitrogen atom. This presumption is corroborated by Riess and his co-workers [7] who have observed the addition of BH_3 to both P and N atoms in a bicyclic phosphane similar to ours. However, the acylic derivatives $R_2NP(OR')_2$, in which the atoms directly bonded to P are the same as in bicyclic phosphanes, addition of BH_3 takes place only on phosphorus.[8]

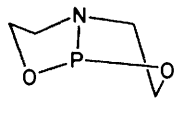
the conformation adopted by each of the four phosphanes studied.



exo-exo

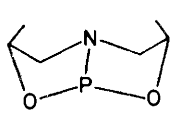


endo-endo

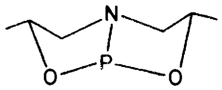


exo-endo

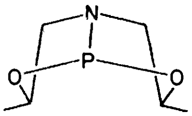
Let us consider first phosphane (2). The two rings A and B, as opposed to those of (3)—(5) are symmetrically substituted. The phosphane studied here is the *meso*-derivative in which the two CH_3 substituents have the same orientation towards the phosphorus and nitrogen lone pairs (*R* or *S* configurations of C-3 or -7). Analysis of its ${}^1H$ n.m.r. spectrum (250 MHz) shows that the N–CH_2 and O–CH protons give only one spectrum of the AMXY (Y = P) type. This implies that there is a symmetry plane containing the P–N bond and the lone pairs. Taking into account the *R* and S configurations of C-3 and -7, the molecule takes on one of the four forms (2*exo–exo*), (2′*exo–exo*), (2*endo–endo*), and (2′*endo–endo*).



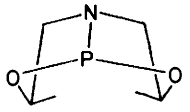
(2 *exo-exo*)



(2′ *exo - exo*)



(2 *endo - endo*)



(2′ *endo - endo*)

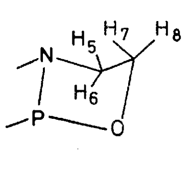
A thorough analysis of molecular models shows that the different interactions between groups and atoms, between the two methyl substituents and between the CH_3 groups and the free lone pairs or the vicinal hydrogen atoms, are minimized in the (2*endo–endo*) structure. We thus propose it as the major diastereoisomer.

The disposition of the protons results from analysis of the ${}^3J$(H-C-C-H) coupling constants: $J_{2,4} = J_{6,8} = 4.5$ Hz can be attributed to *cis*-coupling. Under these conditions, the P–O–C–H-2 (or P–O–C–H-8) and P–N–C–H-3 (or P–N–C–H-5) dihedral angles are close to 90° whereas the P–N–C–H-4 and P–N–C–H-6 dihedral angles are large (close to 150°). If, as is usually assumed, the ${}^3J$(P-X-C-H) coupling constants follow the Karplus law,[9] small $J_{2,\mathrm{P}}$ (or $J_{5,\mathrm{P}}$) constants and large $J_{4,\mathrm{P}}$ (or $J_{6,\mathrm{P}}$) constants must be observed.* This is the case (Table 1). The calculation of the torsional angle around the C–C bond (using the method elaborated by Cazaux and Navech [10]) amounts to 50°.

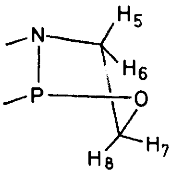
The study of phosphanes (3)—(5) requires separate examination of the A and B rings. As these rings are differently substituted nothing allows us to assume, *a priori*, that they adopt the same conformation.

Non-substituted Ring B Compounds (3) *and* (5).—The values for the ${}^3J$(H-C-C-H) coupling constants, 4.5—6 Hz for *cis*-coupling, 11 and < 1 Hz for *trans*-coupling, confirm, if necessary, the blocking of these rings.

The use of induced chemical shift reagents allowed us to establish that these rings have the *endo*-conformation. Depending on the proton considered, the spectrum of (5), recorded in the presence of $Eu(fod)_3$, shows noticeably different induced chemical shifts. The signal for 7-H, strongly coupled to phosphorus, undergoes a maximum shift of 103 Hz whereas the maximum shift of the signal for 8-H, not coupled to phosphorus, is only 82 Hz. For the N-CH_2 (5- and 6-H) protons the situation is reversed: the signal for 5-H, which is weakly coupled to phosphorus, shows the greatest induced chemical shift. These data are interpreted as follows: whatever the site of complexation of europium (phosphorus or nitrogen), one can expect the signals of the protons which are *cis* to the lone pairs to undergo a larger shift than the *trans*-protons. In the *exo*-conformation, 7-H would be in such a position that the P–O–C–H-7 dihedral angle would be 90°, thus leading to very weak coupling to phosphorus. In the *endo* conformation, the P–O–C–H-7 dihedral angle is close to 150 °C, thus accounting for the large coupling noted between 7-H and P ($J_{7,\mathrm{P}}$ 10.5 Hz). A similar argument can be applied to the N–CH_2 protons.



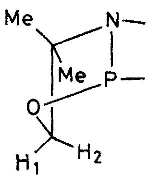
(5 *exo*)



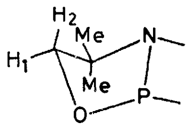
(5 *endo*)

The torsional angles around the C–C bond, calculated as before, are 45° for (3) and 41° for (5).

Substituted Rings.—Compound (3). For ring A, the conformational information comes from the coupling constants of the O-CH_2 protons with phosphorus, giving a large P–O–C–H-1 dihedral angle ($J_{1,\mathrm{P}}$ 14 Hz) and a P–O–C–H-2 dihedral angle close to 90° ($J_{2,\mathrm{P}}$ 0.8 Hz). These data are compatible either with an *endo*-conformation in which 1-H is *cis* to the phosphorus and nitrogen lone pairs, or with an *exo*-conformation where 1-H is *trans*. However the 1- and 7-H have practically the same chemical shift and exactly the same coupling constant with phosphorus. Thus we propose the *endo*-conformation as already proposed for ring B.



(3 *endo*)



(3 *exo*)

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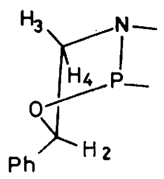
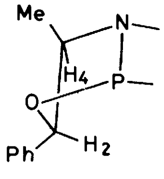
* It is well established that ${}^3J$(P–O–C–H) is markedly dependent on the phosphorus lone pair orientation. Referring to the known effect in 1,3,2-dioxaphosphorinanes, the observed values do not lead to ambiguity in the assignment of CH_2 protons.

Compound (4).—We deal only with the major diastereoisomer obtained in the synthesis. The examination of molecular models shows that the different interactions between groups and atoms are minimized in the *endo*-conformation, the phenyl group (ring A) being ' on the roof '. This justifies, *a posteriori*, the proposition we made when dealing with the stereochemistry. In this conformation, the relative arrangement of 2-, 3-, and 4-H in (4*endo*) perfectly fits the coupling constants. The torsional angle around the C–C bond is 48°.



(4 *endo*)

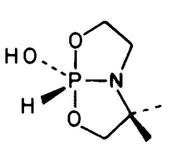


(5 *endo*)

For ring B, we can apply the same reasoning put forward for ring A in (3) with the difference that we lack some comparative elements between the ring A protons and those of ring B. Thus we cannot use the same proposition as for (3).

Compounds (5).—The stereochemistry proposed for ring A of (4) may be equally applied to that of ring A of (5) for which we propose the *endo*-conformation. The torsional angle around the C–C bond is 43°.

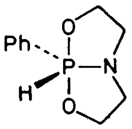
In conclusion, we may state that, with the exception of compound (4) for which there is doubt concerning the conformation of ring **B**, the phosphanes studied have a blocked *endo–endo*-conformation. This blocking is the origin of the strong ring constraints which appear clearly in the molecular model. So any reaction which minimizes this tension will be favoured. Thus oligomerization which needs the breaking of a P–O or P–N bond is quick and easy. In the same way the ability of bicyclic phosphanes to add quickly molecules containing mobile hydrogen can be explained,[*] leading to bicyclic phosphoranes, which are stable structures. The resulting stabilization is so large that we were able to observe, at room temperature, the reactive intermediate, hydroxyphosphorane (8c), with a P–H bond, as a result of the addition, before hydrolysis, of a water molecule to phosphane (3).[13]



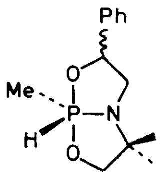
(8c)

It then seemed interesting to compare, from the conformational point of view, bicyclic phosphanes and phosphoranes derived from the same aminodiols.

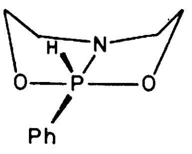
The conformational study of compounds (6a) and (9d)[†] led us to the following conclusions:[14,15] (i) in both derivatives, the nitrogen atom has a planar geometry; (ii) the five-membered rings are blocked in an envelope conformation; and (iii) in phosphorane (6a) the equatorial plane containing C-PH(N) is a symmetry plane of the molecule. The folds of the two envelopes are oriented in the same way. The skeleton of phosphorane (9d) has the P–N bond as a C_2 symmetry axis. The folds of the two envelopes are directed in the opposite way.



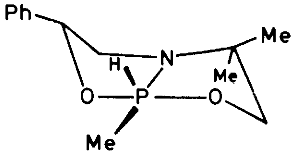
(6a)



(9d)



(6a)



(9d)

Table 2 gives the ^{1}H n.m.r. parameters of phosphanes (2)—(4) and that of the corresponding phosphoranes (7a),[‡] (8a), and (9a).[§]

A careful study of Table 2 shows that the most marked differences between the phosphanes and phosphoranes are to be found in the parameters of the protons α to nitrogen, 3- and 4-H (or 5- and 6-H). For protons α to oxygen, 1-, 2-, 7-, and 8-H, the geminal coupling constants $J_{1,2}$ and $J_{7,8}$ as well as $J_{1,\mathrm{P}}$, $J_{2,\mathrm{P}}$, $J_{7,\mathrm{P}}$, and $J_{8,\mathrm{P}}$ have almost the same value in phosphanes (2)—(4) and in phosphoranes (7a)—(9a). The case is different for the constants associated with 3- and 4-H (or 5- and 6-H), whose values undergo large variations on going from phosphanes to phosphoranes: $J_{3,4}$ changes from -13 and -14 Hz to -7.5 and -8 Hz and $J_{4,\mathrm{P}}$, in particular, from 13 and 15 Hz to 24.0, 26.8, and 29.5 Hz.

Thus the most important conformational differences between phosphanes and phosphoranes are in the P–N–C–H fragment because of the difference in the geometry of nitrogen, tetragonal in phosphanes and planar in phosphoranes.

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[*] There is an important difference between the behaviour towards alcohols of the cage compounds studied by Verkade and of the bicyclic phosphanes. For the former, oxidative addition is not observed, as the basicity of the phosphorus lone pair is measured by the phenol method,[11] whereas for the latter, oxidative addition is instantaneous.[12]

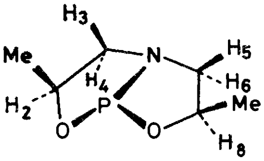
[†] This phosphorane is a mixture of two racemic diastereoisomers. The conformational conclusions stand for both.

[‡] This compound consists of three racemic diastereoisomers in the ratio 80 [δ -42.5 p.p.m. ($J_{\mathrm{H-P}}$ 700.3 Hz)] : 10 [δ -47.1 p.p.m. ($J_{\mathrm{H-P}}$ 689.5 Hz)] : 10 [δ -50.6 p.p.m. ($J_{\mathrm{H-P}}$ 683.3 Hz)]. The major diastereoisomer was studied; the relative dispositions of the methyl substituents and the phenyl group proposed here are the outcome of a critical analysis of the n.m.r. parameters of the P–H group.[16]

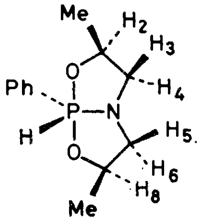
[§] The phosphorane studied here is one of the two expected racemic diastereoisomers, which we have been able to isolate separately.[16]

TABLE 2

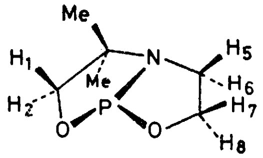
^1H N.m.r. parameters of phosphanes (2)—(4) and phosphoranes (7a)—(9a). Solvent C_6D_6. Frequency 250 MHz



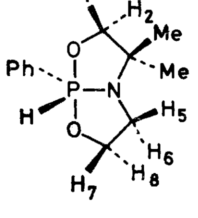
(2)



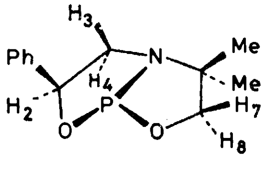
(7a)



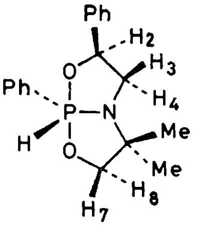
(3)



(8a)



(4)



(9a)

	(2)	(7a)	(3)	(8a)	(4)	(9a)
1-H			3.18	3.46_4		
2-H	3.98	3.71	2.66_4	3.20_8	4.41_2	4.72
3-H	2.72	2.29			2.64	2.55_6
4-H	3.14	2.73			3.20_8	2.86_2
5-H	2.72	2.29	2.36_4	2.59_6		
6-H	3.14	2.73	2.57_8	2.39		
7-H			3.18_4	3.70_4	3.46	3.56_6
8-H	3.98	3.71	2.72_6	3.44_8	3.01_6	3.30_1
$J_{1.2}$			−8	−8.5		
$J_{1.3}$						
$J_{1,4}$						
$J_{1.P}$			14	16.5		
$J_{2.3}$	11	9.5			11	9.6
$J_{2.4}$	4.5	6			4.5	6.3

	(2)	(7a)	(3)	(8a)	(4)	(9a)
$J_{2,P}$	0	0	<0.8	2	0	0
$J_{3,4}$	−13	−8			−14	−8
$J_{3,P}$	0	<1			0	1.5
$J_{4,P}$	13	29.5			15	26.8
$J_{5,6}$	−13	−8	−13	−7.5		
$J_{5.7}$			5.5	6.5		
$J_{5.8}$	11	9.5	11	10		
$J_{5.P}$	0	<1	0	3		
$J_{6,7}$			<1	2		
$J_{6,8}$	4.5	6	4.5	6.5		
$J_{6.P}$	13	29.5	13	24		
$J_{7.8}$			−8	−8.5	−8.5	−8.5
$J_{7.P}$			14	15	15.5	16.7
$J_{8.P}$	0	0	0	2	0.3	1.9

The decrease of the absolute value of $J_{3,4}$ may signify closing of the 3-H–C–C-H angle; the examination of the molecular model shows that such closure leads to a significant increase in the P–N–C–H-4 dihedral angle. This can explain the observed increasing of $J_{4,P}$. One may notice that the torsion around the C–C bond is weaker in the phosphoranes than in the phosphanes: the variations between $^3J_{H-C-C-H}$ *trans* and *cis* are smaller in the former compounds than in the latter; ($J_{2.3}$ − $J_{2.4}$) or ($J_{5.6}$ − $J_{7.8}$) = 3.3 Hz in (7a)—(9a) and 6.5 Hz in (2)—(4). The corresponding torsional angles are 33° in (7a), against 50° in (2), 43° in (8a) against 45° in (3), and 39° in (9a), against 48° in (4). Without putting too much emphasis on these values, we must point out that the variations of these angles are in line with the increase in torsion on going from phosphoranes to phosphanes. This would explain, to an extent, the difference in stability of the two structures.

Conclusions.—The synthesis and conformational study of the bicyclic phosphanes (2)—(5) allows us (i) to define the conditions under which this type of compound can be obtained; (ii) to specify the conformation of oxa-azaphospholan rings, a blocked envelope form, the carbon atoms α to oxygen being located at the tip of the folds; and (iii) to underline that the change in geometry of the nitrogen atom on going from phosphanes to phosphoranes ($sp^3 \longrightarrow sp^2$) has a greater conformational effect than that due to the change in geometry of the phosphorus atom ($sp^3 \longrightarrow sp^3d$).

EXPERIMENTAL

4,4-Dimethyl-2,8-dioxa-5-aza-1-phospha^{III}*bicyclo*[3.3.0]*octane* (3).—A solution of PCl_3 (6.86 g, 0.05 mol) in dry benzene (25 ml) was added over 1 h to a solution of 4,4-dimethyl-3-azapentane-1,5-diol (6.65 g, 0.05 mol) and triethylamine (18 g) in benzene (150 ml), maintained at 0 °C. The mixture was then heated at 40 °C for 6 h. After addition of light petroleum (100 ml), triethylammonium hydrochloride was separated by filtration and the solvent removed. In the first distillation under reduced pressure, a part (about a third) of crude product decomposes. A second distillation gives *product* (3) (35%), b.p. 38—40 °C at 3 mmHg (Found: C, 44.4; H, 7.5; N, 8.3; P, 19.2. $C_6H_{12}NO_2P$ requires C, 44.1; H, 7.5; N, 8.9; P, 19.2%).

3-Phenyl-6,6-dimethyl-2,8-dioxa-5-aza-1-phospha^{III}*bicyclo*-[3.3.0]*octane* (4).—A solution of tris(dimethylamino)phosphane (8.15 g, 0.05 mol) and 1-phenyl-4,4-dimethyl-3-azapentane-1,5-diol (10.45 g, 0.05 mol) in xylene (75 ml) was heated at 140 °C. Dimethylamine was removed by a dry nitrogen flow and titrated by an N-sulphuric acid solution. After 5 h dimethylamine evolved represented 85% of the expected amount. The solvent was removed and two distillations under reduced pressure gave *compound* (4) (5 g, 45%), b.p. 98 °C at 3 mmHg (Found: C, 60.5; H, 6.9; N, 5.9; P, 12.8. $C_{12}H_{16}NO_2P$ requires C, 60.7; H, 6.8; N, 5.9; P, 13.05%).

3-*Phenyl*-4-*methyl*-2,8-*dioxa*-5-*aza*-1-*phospha*^{III}*bicyclo*-[3.3.0]*octane* (5).—This compound was prepared from $(Me_2N)_3P$ and 1-phenyl-2-methyl-3-azapentane-1,5-diol [16] as before in 45% yield, b.p. 98—102 °C at 3 mmHg, *m/e* 223 (M^+) (Found C, 58.8; H, 6.3; N, 6.3; P, 13.6. $C_{11}H_{14}NO_2P$ requires C, 59.2; H, 6.3; N, 6.25; P, 13.9%).

Instrumentation.—^{31}P N.m.r. spectra were recorded on Perkin-Elmer R10 (continuous wave mode) and Perkin-Elmer R32 (Fourier transform mode) instruments with an 85% H_3PO_4 solution as an external standard. Chemical shifts are positive to low field. ^1H N.m.r. spectra were obtained on Varian T 60, H.A. 100, and Cameca 250 instruments using tetramethylsilane as internal standard.

We thank Dr. J. Navech, Maître de recherche au C.N.R.S., who calculated the torsional angles. We are also indebted to Mrs. M. Bon and Mr. J. P. Beteil, Groupement Régional des Mesures Physiques de Toulouse, for recording 250 MHz ^1H n.m.r. spectra, and to Dr. J. C. Promé, Maître de recherche au C.N.R.S., and Mr. J. Roussel for recording mass spectra.

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