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CYCLIC ORGANOPHOSPHORUS COMPOUNDS—V[1]

HIGH RESOLUTION NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOME 5,5-DIALKYL-1,3,2-DIOXAPHOSPHORINANES AND RELATED COMPOUNDS

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Abstract—Proton chemical shifts, and ^{31}P–^{1}H coupling constants through sequences of 1,2,3, and 4 chemical bonds, are reported for the 5,5-substituted-1,3,2-dioxaphosphorinanes (I: X = O or S; R_1 = R_3 = Me or Et; R_1 = Me, R_3 = $ClCH_2$; R_3 = alkyl, alkoxy, aryloxy, alkylamido, halogeno, H,). In some cases, the 4,6-methylene hydrogen resonances have been analysed by means of an ABX approximation.

Comparison of the ^{31}P spectra of the esters (I: R_1 = R_3 = Me; X = O, S; R_3 = OMe) with that of a monothiopyrophosphate indicates that the latter has the structure (II: X = S; Y = Z = O) rather than (II: X = Z = O; Y = S).

ALTHOUGH NMR spectroscopy can provide useful information about conformational aspects of organic ring systems,[2] it has been applied only recently to ring systems containing phosphorus. Many more studies have been carried out on five-membered monocyclic[3,4] and polycyclic[5–9] phosphorus compounds than on six-membered monocyclic compounds.[10,11]

Six-membered rings with at least three adjacent, unsubstituted methylene groups may give rise to complex NMR spectra. However, these may be simplified by replacing the hydrogens of the centre methylene group. Thus, geminally substituted compounds have proved to be easier subjects for NMR studies,[12] as we found in our examination of 5,5-disubstituted-1,3,2-dioxaphosphorinanes. Many 5,5-dimethyl-2-oxo- and 5,5-dimethyl-2-thiono-1,3,2-dioxaphosphorinanes have been described

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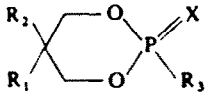
previously,[13–17] and stereospecific formation of closely related compounds has been shown to take place using 4-alkyl-2,6,7-trioxa-1-phosphabicyclo(2,2,2)octanes in the Arbuzov reaction.[8,18]

The preparation of some new 5,5-dimethyl- and 5,5-diethyl-2-oxo-1,3,2-dioxaphosphorinanes is described. The methods used, were (a) interaction of a phosphonic dichloride and the requisite diol in the presence of pyridine (I: X = O; $R_1 = R_2 =$ Me; $R_3 = CCl_3$, sec. Bu, t-Bu, CHMePh), (b) via the Arbuzov reaction using 5,5-dimethyl-2-methoxy-1,3,2-dioxaphosphorinane (giving I: $R_1 = R_2 =$ Me; $R_3 =$ Me, CH_2Ph, CPh_3; X = O) or 4-methyl-2,6,7-trioxa-1-phosphabicyclo(2,2,2)octane (giving I; X = O; $R_1 =$ Me, $R_2 = ClCH_2$; $R_3 = CH_2Ph$), and (c) from the cyclic phosphorochloridate with an alkylamine or metal alkoxide (giving I: X = O, $R_1 = R_2 =$ Me; R_3 = OBu-tert; X = O, $R_1 = R_2 =$ Et, R_3 = OPr-iso, NHBu-t.).



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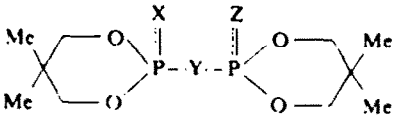

II

EXPERIMENTAL

Materials. General experimental details are as outlined in previous papers in this series. M.ps are uncorrected.

5,5-*Dimethyl*-2-*oxo*-2-*triphenylmethyl*-1,3,2-*dioxaphosphorinane*. Reaction between triphenylmethylphosphonic dichloride[19] and 2,2-dimethylpropane-1,3-diol in the presence of pyridine in boiling toluene yielded none of the required phosphonate.

5,5-Dimethyl-2-methoxy-1,3,2-dioxaphosphorinane (3·3 g; prepared by transesterification between trimethyl phosphite and 2,2-dimethylpropane-1,3-diol) and triphenylmethyl chloride (5·5 g) were heated together. At 140°, evolution of MeCl commenced and, after 4 hr at the same temp, the mixture became solid. The heating was continued for a further hr, and the cooled product was triturated with EtOH, and the residue crystallized from the same solvent. The *compound* (5·3 g, 67%) had m.p. 211·5–212°. (Found: C, 73·55; H, 6·3; P, 8·15. $C_{24}H_{25}O_3P$ requires: C, 73·45; H, 6·4; P, 7·9%.)

2-*Benzyl*-5,5-*dimethyl*-2-*oxo*-1,3,2-*dioxaphosphorinane*. This (60%), m.p. 105·5–106° (from cyclohexane), was prepared by essentially the same procedure. The reaction mixture was heated for 12 hr at 170–180°. (Found: C, 60·0; H, 7·1; P, 13·15. $C_{12}H_{17}O_3P$ requires: C, 60·0; H, 7·15; P, 12·9%.)

2-*Oxo*-2,5,5-*trimethyl*-1,3,2-*dioxaphosphorinane*. This compound has previously been recorded[19] but it has now been obtained in better yield by a modified procedure.

5,5-Dimethyl-2-methoxy-1,3,2-dioxaphosphorinane (4·0 g) and NaBr (0·5 g) were stirred together

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at 70° for 18 hr. The residue was extracted with boiling AcOEt from which the compound (1·3 g) separated.

5-Chloromethyl-5-methyl-2-oxo-2-triphenylmethyl-1,3,2-dioxaphosphorinane. This, m.p. 190–191° (from EtOH; lit. m.p. 201°) was prepared as described by Verkade *et al.*[19]

2-Benzyl-5-chloromethyl-5-methyl-2-oxo-1,3,2-dioxaphosphorinane. This was obtained by heating together benzyl chloride (2·5 g) and 4-methyl-2,6,7-trioxa-1-phosphabicyclo(2,2,2)octane (3·0 g) at 170° and 12 hr. The resulting crude product was chromatographed on silica and eluted with benzene–ether, 2:3. The *product*, (0·5 g, 10%) had m.p. 156·5–157° (from CCl_4). (Found: C, 52·25; H, 5·9; P, 11·35. $C_{12}H_{16}ClO_3P$ requires: C, 52·45; H, 5·9; P, 11·3%.)

5,5-Dimethyl-2-oxo-2-trichloromethyl-1,3,2-dioxaphosphorinane. Trichloromethylphosphonic dichloride (10·3 g) was added portionwise to 2,2-dimethylpropane-1,3-diol (5·3 g) and pyridine (7·9 g) in benzene (25 ml). The reaction was exothermic. The mixture was allowed to stand for 1 hr, and then heated over steam for 1 hr. The cooled soln was washed with water, $KHCO_3$aq (100g per l.), and dried. Evaporation of the soln and crystallization of the residue from benzene yielded the *compound* (7·7 g, 58%) m.p. 168–169°. (Found: C, 26·95; H, 4·05; P, 11·55. $C_6H_{10}Cl_3O_3P$ requires: C, 26·95; H, 3·8; P, 11·6%.)

2-t-Butyl-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane. A mixture of 2,2-dimethylpropane-1,3-diol (5·4 g), pyridine (7·9g) and t-butylphosphonic dichloride (8·7 g) in toluene (25 ml) was refluxed for 13 hr. The soln was worked up as in the previous example. The *compound* (3·1 g, 30%) had m.p. 164–165° (from benzene–petroleum ether). (Found: C, 52·5; H, 9·1; P, 15·3. $C_9H_{19}O_3P$ requires: C, 52·4; H, 9·3; P, 15·0%.)

5,5-Dimethyl-2-oxo-2-α-phenylethyl-1,3,2-dioxaphosphorinane. This, m.p. 120–122° (from ether) will be described elsewhere.[20]

2-sec-Butyl-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane. This, m.p. 60° (from pet ether) will be described elsewhere.[20]

5,5-Dimethyl-2-dimethylamino-1,3,2-dioxaphosphorinane. This, (57%), b.p. 64–66°/6 mm, was prepared in the conventional manner from the cyclic phosphorochloridite[14] and dimethylamine in ether. (Found: C, 47·6; H, 8·8; P, 17·7. $C_7H_{16}NO_3P$ requires: C, 47·5; H, 9·0; P, 17·5%.)

5,5-Dimethyl-2-dimethylamino-2-thiono-1,3,2-dioxaphosphorinane. This, m.p. 73–73·5° (from pet ether, b.p. 40–60) was obtained in theoretical yield by addition of S to the above cyclic phosphoramidite. (Found: C, 40·2; H, 7·55; P, 15·0. $C_7H_{16}NO_3PS$ requires: C, 40·2; H, 7·7; P, 14·8%.)

2-t-Butoxy-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane. Solid sodium t-butoxide (from 1·15 g Na) was suspended in ether (100 ml). 2-Chloro-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane (9·3 g) was added in portions during 1 hr. The mixture was refluxed for 6 hr, washed with water and dried. The solvent was removed to leave the *ester* (5·9 g, 53%), m.p. 78–79° (dec) (from pet ether). (Found: C, 48·6; H, 8·6; P, 14·7. $C_9H_{19}O_4P$ requires: C, 48·65; H, 8·6; P, 13·95%.)

2-Chloro-5,5-diethyl-2-oxo-1,3,2-dioxaphosphorinane. A mixture of 2,2-diethylpropane-1,3-diol (26·4 g), pyridine (31·6 g) and $POCl_3$ (31 g) in benzene (200 ml) was heated at 60° for 1 hr, and worked up in the usual way to give the cyclic phosphorochloridate b.p. 161–167°/4 mm, (lit.[21] m.p. 42·5–44·5°), which slowly solidified. (Found: P, 14·15. Calc. for $C_7H_{14}ClO_3P$: P, 14·5%.)

5,5-Diethyl-2-isopropoxy-2-oxo-1,3,2-dioxaphosphorinane. A mixture of the above cyclic phosphorochloridate (4·6 g) and solid sodium isopropoxide (from 0·5 g Na) in benzene (20 ml) was refluxed for 3 hr and worked up in the usual way. The *ester*, (1·6g, 32%) has b.p. 136–138°/0·4 mm, n_D^{21} 1·4460. (Found: C, 50·9; H, 8·95; P, 13·1. $C_{10}H_{21}O_4P$ requires: C, 50·85; H, 8·7; P, 12·9%.)

2-t-Butylamino-5,5-diethyl-2-oxo-1,3,2-dioxaphosphorinane. Prepared from the cyclic phosphorochloridate (2·1 g), and t-butylamine (1·5 g) in boiling benzene (10 ml). The *amide* (2·4 g, 95%) had m.p. 126–126·5° (from benzene–pet ether). (Found: P, 12·6. $C_{11}H_{24}NO_3P$ requires: P, 12·45%.)

Spectroscopy. All ^1H spectra were recorded at 60 Mc/s and with r.f. level about 0·2 mG on a Varian A-60 spectrometer, at room temp, unless otherwise specified. Chemical shifts were measured with respect to internal TMS. Most measurements were made with *ca.* 10% solns in CCl_4 or $CDCl_3$, but other solvents are indicated where used.

^{31}P spectra were recorded for Chf solns at 23·3 Mc/s in an r.f. field corresponding to 1 mV on a Perkin–Elmer R 10 spectrometer with P_4O_6 as reference.

[20] R. S. Edmundson and E. W. Mitchell, to be published.
[21] U.S. Pat. 2,892,862 (Union Carbide and Carbon Corp.).

TABLE 1. CHEMICAL SHIFTS (IN ppm DOWNFIELD FROM TMS) AND COUPLING CONSTANTS (IN c/s) FOR CYCLIC PHOSPHONATES. (I: X=O) ALL MEASUREMENTS ARE IN $CDCl_3$ SOLUTION. FOR THE 4,6 PROTONS, PARAMETERS FROM AMX ANALYSES ARE GIVEN IN PARENTHESES IMMEDIATELY BELOW THE CORRESPONDING ABX ANALYSIS PARAMETERS

Ref.	Substituents R_1	R_2	R_3	5-methyl protons narrow	broad	CH_2Cl shifts	4,6 protons δ_A	δ_B	$\lvert J_{AB}\rvert$	$\lvert J_{AX}\rvert$	$\lvert J_{BX}\rvert$	C_6H_5	R_3 shifts Others	^{31}P-R_3 coupling
1·1	Me	Me	Me	1·01	1·11		4·18	3·82	11·5	9·9	14·0		Me 1·57	17·9
				(1·1 c/s)	(1·25 c/s)		(4·22	3·80	11·5	10·2	13·6)			
1·2	Me	Me	CMe_3	0·87	1·25		4·35	3·70	11	2	19		P–C–Me 1·27	16·8
1·3	Me	Me	CPh_3	0·98	0·78		4·27	3·48	11·3	6·6	14·7	7·15 7·65		
				(1·3 c/s)	(1·5 c/s)						or			
											15·7			
							4·27	3·52	11·3	6·8	14·9			
1·4	Me	CH_2Cl	CPh_3		0·80(1·1 c/s)	3·68	4·33	3·42	11·2	11·8	10·7	7·2–7·7		
							(4·33	3·40	11·2	9·9	11·2)			
1·5	Me	Me	CH_2Ph	0·95	0·81		4·17	3·70	11·2	7·8	14·9	7·3	CH_2Ph 3·28	22·1
				(1·1 c/s)	(1·4 c/s)		(4·18	3·68	11·2	8·1	14·7)			
1·6	Me	CH_2Cl	CH_2Ph		0·85(1·0 c/s)	3·58	4·32	3·78	11·6	12·0	11·0	7·34	CH_2Ph 3·33	21·7
							(4·32	3·77	11·6	11·6	10·1)			
1·7	Et	CH_2Cl	CH_2Ph		- -	3·57	3·4 —4·5		11	11	11	7·32	CH_2Ph 3·32	21·5
			Ph											
			/	0·90	0·83									
1·8	Me	Me	CH				3·0 - -4·4					7·34	CHMe 1·65 J_{Me-CH} 7·6	18·6
			\	(1·1 c/s)	(1·3 c/s)									
			Me											
1·9	Me	Me	CHMeEt		0·93		4·25	3·77	10·9	5·2	15·4	15 protons from R_1 R_2 R_3 in 0·85–1·5		
					1·19		(4·27	3·75	10·9	6·0	15·9)	ppm region		
1·10	Me	Me	CCl_3	0·99	1·42		3·94—4·8							

TABLE 2. CHEMICAL SHIFTS (IN ppm) AND COUPLING CONSTANTS (IN c/s) FOR CYCLIC PHOSPHATES AND A THIOPHOSPHATE

Ref.	Substituents X	R_1	R_2	R_3	5-methyl protons narrow	broad	4,6 protons	Me	R_3 shifts CH	Ph	CH_3	R_3 couplings CH—CH_3	P—O—CH	P—O—C—CH	Solvent
2·1*	O	Me	Me	OMe	0·88	1·20	3·5–4·2	3·9 ±					11·0		CCl_4
					0·90	1·24		0·1							$CDCl_3$
2·2	O	Me	Me	OCH_2Me	0·91	1·25		1·37			4 ± 0·3	7		(<1)	CCl_4
2·3	O	Me	Me	$OCHMe_2$	0·90	1·21	3·5–4·5	1·32	4·6			6·5	(6·5)		CCl_4
					0·89	1·25		1·37	4·7						$CDCl_3$
2·4	O	Et	Et	$OCHMe_2$	(complex 0·6–1·9)		3·3–4·3	1·36	4·7			6·0	(6·0)		$CDCl_3$
2·5	O	Me	Me	$OCMe_3$	0·90	1·21	3·6 4·6	1·52						(<1)	$CDCl_3$
2·6	O	Me	Me	OPh	0·97	1·29	3·5–4.45			7·28					$CDCl_3$
2·7†	S	Me	Me	OMe	0·91	1·22	3·6–4·2	3·79					13·9		$CDCl_3$

Coupling constants given in parentheses have been determined indirectly.
* ^{31}P resonance is 50 c/s wide at 119·3 ppm upfield from P_4O_6 (Chf sol).
† ^{31}P resonance is 50 c/s wide at 49·5 ppm upfield from P_4O_6 (Chf sol).

TABLE 3. CHEMICAL SHIFTS (IN ppm) AND COUPLING CONSTANTS (IN c/s) FOR CYCLIC PHOSPHORAMIDATES AND PHOSPHORAMIDOTHIONATES IN $CDCl_3$ SOLUTION

Ref.	Substituents X	R_1	R_2	R_3	5-methyl protons narrow	broad	Other R_3 shifts	4,6 protons δ_A	δ_B	$\lvert J_{AB}\rvert$	$\lvert J_{AX}\rvert$	$\lvert J_{BX}\rvert$	R_3 shifts NH	Me	CH	R_3 couplings P–R_3	CH–Me
3·1	O	Me	Me	NH–CMe_3	0·98	1·16	—	4·22	3·85	11·2	7·8	16·3	2·95	1·23		0·8	
3·2	O	Et	Et	NH–CMe_3	complex in range 0·6 1·8			4·20	3·90	11·1	8·0	16·5	2·6	1·30		0·9	
3·3	O	Me	Me	NH–$CHMe_2$	0·90	1·17 ± 0·06	—	3·1–4·5					3·2	1·17	3·1–4·5		J_{CH-Me} 6·5
3·4	S	Me	Me	NH–$CHMe_2$	0·85	1·24	--	3·2–4·6					3·5	1·20	3·2–4·6		$J_{CH\ Me}$ 5·5
3·5	S	Me	Me	N–Me_2	0·91	1·25	--	4·30	3·77	11·2	6·2	22·4	--	2·83		12·0	
								(4·32	3·75	11·2	6·0	22·2)					

TABLE 4. CHEMICAL SHIFTS (IN ppm) AND COUPLING CONSTANTS (IN c/s) FOR MISCELLANEOUS 5,5-DIMETHYL DIOXAPHOSPHORINANES

Ref.	Substituents X	R_a	5-methyl protons narrow	broad	4,6 protons	R_a shift	P-R_a coupling	Solvent
4·1	O	H	0·94	1·28	3·6–4·6	6·88	675	$CDCl_3$
4·2	S	H	0·94	1·27	3·65–4·3	7·68	600	CCl_4
			0·91	1·28	3·5–4·3	7·77	601	$CDCl_3$
4·3	O	Cl	0·93	1·32	3·6–4·4	- -	- -	$CDCl_3$
4·4	S	Cl	0·91	1·32	3·5–4·4	- -	- -	CCl_4
4·5	S	SH	1·15* (singlet)		4·06* (doublet) J_{POCH_3} 15·5	3·25*	—	$CDCl_3$
4·6	S	SD†	1·13		4·08 (doublet) J_{POCH_3} 15·5	2·85	—	$CDCl_3$

* Similar values at −55°.
† Containing 25% H.

TABLE 5. CHEMICAL SHIFTS (IN ppm) AND COUPLING CONSTANTS (IN c/s) FOR PYROPHOSPHATES

Ref.	X	Y	Z	5-methyl protons narrow	broad	4,6 protons	Solvent
5·1	O	O	O	0·93	1·35	3·67–4·70	$CDCl_3$
5·2†	S	S	S	0·89	1·2 ± 0.1	too weak	$(CD_3)_2SO$
5·3*	O	O	S	0·91	1·32	3·60–4·75	$CDCl_3$
5·4	S	S	O	0·92 (2·0 c/s)	1·34 (2·5 c/s)	3·6–4·8	$CDCl_3$
5·5†	S	O	S	0·93	1·32	3·7–4·7 (weak)	$CDCl_3$
	S	O	S	0·85	1·19	too weak	$(CD_3)_2SO$

* ^{31}P resonance is quartet (28 c/s splitting) at 68·5 and 136·5 ppm upfield from P_4O_6 (Chf soln).
† Soln very dilute because of poor solubility.

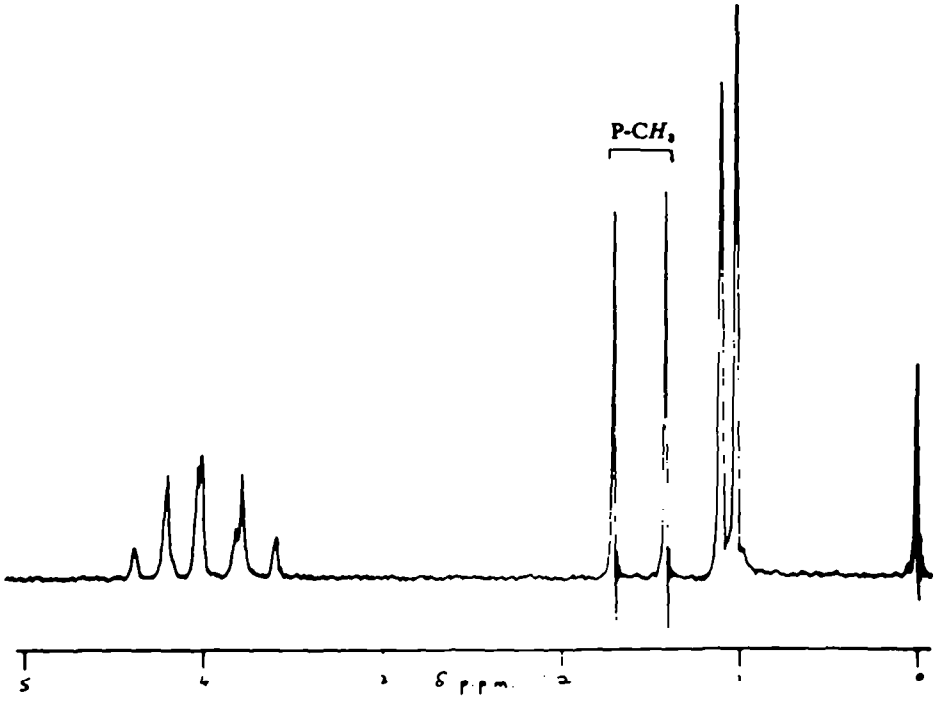

FIG. 1. PMR spectrum of 2-oxo-2,5,5-trimethyl-1,3,2-dioxaphosphorinane.

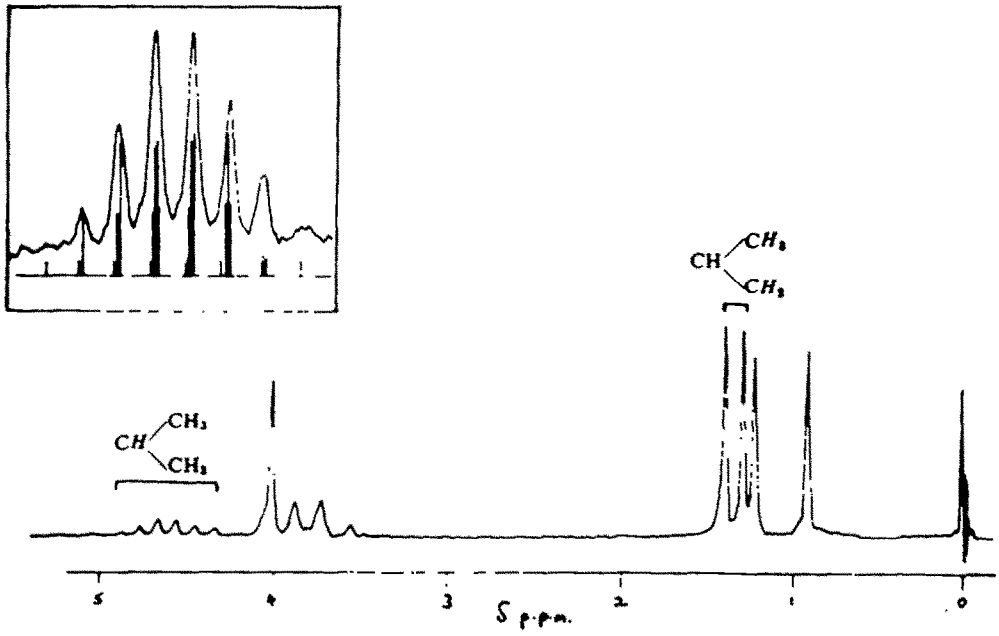

FIG. 2. PMR spectrum of 5,5-dimethyl-2-isopropoxy-2-oxo-1,3,2-dioxaphosphorinane. Inset: resonance of *CH* of isopropyl group.

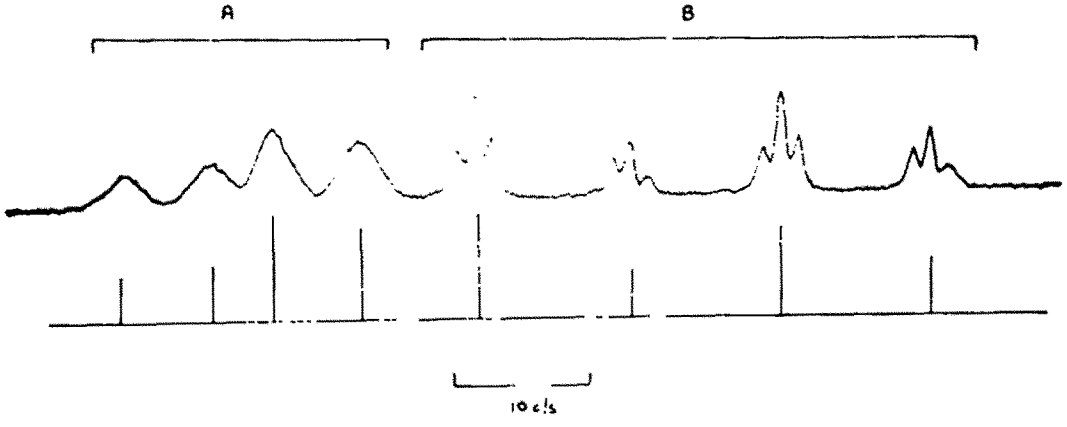

FIG. 3. Resonance of 4,6-protons of 5,5-dimethyl-2-dimethylamino-2-thiono-1,3,2-dioxaphosphorinane, with calculated AB part of ABX system.

RESULTS

General form of nuclear resonance spectra. Strictly, all the NMR spectra are of very complex spin systems. For example, the system for spectrum 1·10 (Table 1) might formally be described as $AA'BB'K_3Q_3X$, where A, B are 4,6 hydrogens, K and Q are Me hydrogens, and X is the phosphorus; in many of the compounds, the phosphorus is further coupled to protons in the R_5 group. However, in view of the small magnitudes found for the couplings $J_{AA'}$ and $J_{BB'}$, across the ring, and from the 4,6-protons to the 5-Me protons, in comparison with couplings J_{AB}, J_{AX} and J_{BX}, we

frequently approximate these systems to ABX or AMX.[22] Thus the ^1H spectrum of the typical 5,5-dimethyl-1,3,2-dioxaphosphorinane (Fig. 1) consists of: (i) very slightly broadened axial and equatorial 5-methyl peaks near 1·2 and 1·0 ppm respectively; (ii) an approximation to the AB part of an ABX system from the 4,6 protons in the range 3·4–4·8 ppm; and (iii) additional —C*H*, —N*H*, methyl, etc., peaks, according to the nature of the R_3 group, usually with further coupling to the phosphorus.

The NMR spectral data are summarised in Tables 1–5. The following remarks amplify these for certain groups of compounds; more general points are covered in the Discussion.

Cyclic phosphates (Table 2). In the 4,6-proton region, spectra 2·3 (Fig. 2), 2·4 and 2·5 have what are taken to be deceptively simple forms, with an intense narrow peak at 4·05 ppm and an apparent quartet centred on 3·8 ppm; they were not suitable for ABX analyses.

In spectrum 2·3, methine-methyl coupling within R_3 gives a 6·5 c/s doublet for the Me protons; the corresponding 6·5 c/s septet for the methine proton is complicated by phosphorus coupling to give a sequence of observed relative intensities: 1·3:4·6: 8·9:8·3:5·3:2·6:1·0. In accounting for the methine resonance, ^{31}P coupling to the 4,6-protons may be neglected so that the spin system may be regarded as A_6BX. As an approximation, the B part of this has been calculated by superposing two B parts of A_6B systems,[23] in each of which there are 16 non-zero lines and the ratio $J_{AB}/\nu_{AB} = 0{\cdot}25$. Comparison of calculated spectra for J(P—O—CH) equal to J_{AB} and to 2 J_{AB} indicated that the ^{31}P—O—CH coupling was near 6·5 c/s rather than 13 c/s. An analogous situation holds for spectrum 2·4 except that the first order septets are out of register. In 2·1, on the other hand, the positions of the three sharp peaks of approximately equal intensity in the 3·7–4·1 ppm region show that P—O—CH_3 coupling must be 11 c/s. In this spectrum, the pair of lines of the ^{31}P-split R_3-Me is superposed on a fortuitously simple 4,6-proton region of the kind shown by spectrum 2·3. The many lines to be expected in the ^{31}P resonance of 2·1 are not resolved; a 50 c/s wide band is observed 119·3 ppm upfield from P_4O_6.

Miscellaneous dioxaphosphorinanes (Table 4). While the fortuitous simplicity of the 4,6-proton region in the spectra of the cyclic phosphates (Fig. 2) is not maintained, there is again one very intense component of the AB part of the ABX system at 4·2 ppm.

Large direct P–H splittings were measured for spectra 4·1 and 4·2. Despite the simplicity of the R_3 groups, it is noticeable that, except for 4·5 and 4·6, all of these spectra show the distinct axial and equatorial 5-Me peaks to be expected from rigid conformations. Apart from some broadening of the lines, the general form of the spectrum 4·5 did not change when the temperature was reduced to −55°. There is a surprisingly large solvent effect on the appearance of the 4,6-proton resonances of compound 4·2. In CCl_4, a quartet of broad lines centred at 4·05 ppm is replaced by a very sharp, intense band at 4·2 ppm plus a multiplet at 3·5–4·1 ppm when $CDCl_3$ is the solvent.

Bicyclic pyrophosphates (Table 5). In ^1H resonance, all the compounds show axial/equatorial pairs of 5 and 5′ Me protons at the expected positions of about 0·92

[22] An analogous approximation as ABX in an aromatic ring proved satisfactory in *p*-substituted triarylphosphines.[24]

[23] J. Ranft, *Ann. der Physik* **10**, 1 (1962).

(narrow) and 1·33 ppm (broad) in $CDCl_3$ solutions; those measured in deuterated DMSO, because of low solubility, are shifted upfield slightly. Methyl line-widths of the symmetrical molecules are only slightly broader that in the corresponding monocyclic compounds. The very slight extra broadening from 1·5 and 2·0 c/s to 2·0 and 2·3 c/s in the symmetrical bicyclic pyrophosphates shows that the chemical shifts of the 5 and 5′ methyls must be only slightly influenced by the atoms X, Y, and Z. Similarly, the methylene protons seem little affected by the composition of the bridge region; for spectrum 5·4, eight lines of the AB part (J_{AB} = 11 c/s) of the methylene system are well resolved. Each is broadened to about 4 c/s and shows signs of structure, possibly because of coupling to at least one of the 5,5′ Me groups.

In compound 5·3, one might expect ^{31}P resonance to give an AB system, from the chemically different phosphorus nuclei, split by coupling to the formally different sets of axial/equatorial 4,6,4′,6′ protons. In fact, rough quartets of 28 c/s splitting are resolved at 68·5 and 136·5 ppm upfield from P_4O_6. These shifts are quite close to the values of 49·5 and 119·3 ppm measured in the relevant monocyclic 1,3,2-dioxaphosphorinanes 2·7 and 2·1, respectively, and helped to confirm the asymmetrical arrangement in the monothiopyrophosphate, (II:X = S; Y = Z = O).[24] In the isohypophosphate ion, phosphorus-phosphorus splitting amounts to 17 c/s.[25]

DISCUSSION

Examination of the 5-methyl protons. In most of the spectra in all the Tables, the 5,5-dimethyl resonances consist of one relatively narrow (1·0–1·1 c/s) peak at about 0·90–0·95 ppm and a slightly broader peak (1·2 c/s) at about 0·3 ppm higher field. For spectra of compounds with a direct P—C linkage (Table 1) however, this sequence is sometimes reversed (spectra 1·3, 1·5, 1·8) or indeterminate (spectrum 1·9). High-field singlet resonances are obtained in spectra 1·4, 1·6 and relatively low-field singlet spectra in 4·5, 4·6. In the cyclic phosphates (Table 2), there is no significant change in the 5-Me shifts along the R_3 sequence, —Me, —CH_2Me, —$CHMe_2$, —CMe_3, but in the cyclic phosphonates (Table 1) the axial/equatorial shift is appreciably smaller with R_3 = Me than with R_3 = CMe_3.

In the 5,5-dimethyl phosphonates (Table 1), the width of the 5-Me resonance in the 5-methyl-5-chloromethyl compound is 1·1 c/s (spectrum 1·4) compared with widths of 1·3 and 1·5 c/s in the 5,5-dimethyl compound (spectrum 1·3) for R_3 = CPh_3; with R_3 = CH_2Ph, the corresponding values are 1·0 c/s (spectrum 1·6) and 1·1 and 1·4 c/s (spectrum 1·5).

In all cases, the axial and equatorial peaks have a significantly lower height and measurably greater breadth than otherwise comparable three-proton peaks split only by phosphorus. For example, in spectrum 3·5, the 5,5-dimethyl peaks are broadened to 1·3 and 1·8 c/s, compared with 1·1 c/s for the N-Me peaks, and in spectrum 1·1, the dimethyl peaks are 1·2 and 1·0 c/s wide compared with 0·6 c/s for the P-Me peaks.

Evidently, there is unresolved long-range coupling of the 5-Me protons to each other and/or the 4,6-protons. In substituted 1-methylcyclohexanols made rigid by a bulky 4-substituent, it has been found[26] that enhanced long range coupling to the axial

[24] An analogous situation has been shown to exist in the case of tetraethyl monothiopyrophosphate. R. A. Y. Jones, A. R. Katritzky and J. Michalski, *Proc. Chem. Soc.* 321 (1959).

[25] C. F. Collis, J. R. van Wazer, J. N. Shoolery and W. A. Anderson, *J. Am. Chem. Soc.* 79, 2719 (1957).

[26] C. W. Shoppee, F. P. Johnson, R. E. Lack and S. Sternhell, *Chem. Comm.* 347 (1965).

2,6-protons caused the axial Me peak to broaden to 1·0–1·3 c/s as compared with 0·6–0·7 c/s for the corresponding equatorial Me signal. For the cyclic organophosphorus compounds of the present series without a bulky R_3 group, the six-membered rings are also presumed to be only slightly distorted, and it seems plausible to assign the broader Me resonance as axial; thus CH_3 (ax.) would resonate at lower field than CH_3 (eq.).

Examination of the 4,6-*methylene protons.* Despite the formal complexity of the systems, solutions were obtained for many of the spectra as AB parts of ABX systems and the parameters are listed in Tables 1 and 3. In a number of cases, the A and B protons resonate at sufficiently different shifts (non-overlapping lines) for the AMX approximation to be appropriate; the corresponding parameters are listed in parentheses in the Tables.

An ABX analysis may be subject to ambiguities. Thus, in general, it is impossible to determine the sign of J_{AB}, and the relative signs of J_{AX} and J_{BX} can be found only when J_{AB}/δ_{AB} is not too small. An additional ambiguity arose in some cases because the assignment of AB sub-spectra could not be checked from the X part of the spectrum. Even where the ^{31}P spectrum was available (see footnote to Table 2), additional R_3 couplings broadened the line to 50 c/s so as to mask the individual X components. Often, better intensity agreement was obtained with one of the two sets of parameters, ν_A, ν_B, $|J_{AX}|$, $|J_{BX}|$, so that the other set could be rejected.

As Tables 1 and 2 show, axial-equatorial couplings are 11–11·5 c/s, whereas phosphorus couplings to the 4,6-protons range widely from 5 (or even less) to 22 c/s. In cases where the axial 5-Me resonance can be assigned, as suggested in the preceding section, the planarity of the axial Me/axial methylene zig-zag enables the coupling constants J_{AX}, J_{BX} to be correctly associated with ^{31}P coupling to axial or equatorial 4,6-protons. In this way the chemical shifts δ_A and δ_B can themselves be assigned to axial or equatorial protons. For example, in spectrum 3·5 (Fig. 3) the A and B lines of the ABX spectrum do not overlap. Cross-ring coupling causes each B line to appear as a triplet whereas each A line is merely broadened, presumably because further coupling to the 5-methyls is stronger for the A protons. Accordingly, δ_A can be ascribed to axial and δ_B to equatorial methylene protons in this compound.

Among other spectra, for which ABX and/or AMX calculations were made, less marked, but analogous, differences are evident between the A and B lines in spectra 1·1, 1·5 and 3·1, so that again δ_A can be assigned to axial or δ_B to equatorial 4,6-protons. In spectra 1·3, 1·4, 1·7, 1·9 and 3·2, on the other hand, the broadenings of the two groups of lines are about the same.

Phosphorus coupling constants. The spectra discussed in this paper provide further evidence that phosphorus–hydrogen spin–spin coupling constants in organophosphorus compounds parallel those observed for hydrogen–hydrogen couplings, and that the magnitudes of $J(^{31}P, ^1H)$ are usually greater than those of the corresponding $J(^1H, ^1H)$.[27–29] We find values ranging from 675 c/s for J(P—H) in spectrum 4·1, to 0·8 c/s for J(P—N—C—C—H) in spectrum 3·1.

In contrast with the observations of Hendrickson *et al.*,[27] J(P—C—H) (17·9, 22·1,

[27] J. B. Hendrickson, M. L. Maddox, J. J. Sims and H. D. Kaesz, *Tetrahedron* **20**, 449 (1964).
[28] C. E. Griffin, *Tetrahedron* **20**, 2399 (1964).
[29] C. E. Griffin and M. Gordon, *J. Organometall. Chem.* **3**, 414 (1965).
C. E. Griffin, R. B. Davison and M. Gordon, *Tetrahedron* **22**, 561 (1966).

21·7, 21·5, c/s in spectra 1·1, 1·5, 1·6, 1·7 respectively) is, on average, greater than J(P—C—C—H) (16·8, 18·6 c/s in spectra 1·2, and 1·8). While Boros *et al.*[9] report J(P—O—C—C—H) values of about 6 c/s in the rigid boat rings of 2,6,7-trioxa-1-phosphabicyclo(2,2,2)octane and related compounds, we find quite small (<1 c/s) values for J(P—O—C—C—H) (spectra 2·2 and 2·5) and for J(P—N—C—C—H) (spectra 3·1 and 3·2) more in line with the near zero J(P—C—C—C—H) couplings reported by Hendrickson in aliphatic chains. Within the R_3 groups, values of J(P—Y—C—H) show some similarities; for Y = C: J = 16·3 and 18·6 c/s (spectra 1·2 and 1·8); Y = O: J = 12·5, 11·5 and 13·9 c/s (spectra 2·1, 2·4, 2·7); Y = N: J = 12·0 c/s (spectrum 3·5).

In the spectra 1·1, 1·5 and 3·1 of 5,5-dimethyl compounds for which 4,6 protons have been assigned, Tables 1 and 3 show that the coupling constants $J(PO—O—CH)_{ax}$ are in the range 7·8–10 c/s and $J(PO—O—CH)_{eq}$ are in the range 13·8–16·3 c/s. For the phosphoramidothionate in spectrum 3·5, $J(PS—O—CH)_{ax}$ is 6·2 c/s and $J(PS—O—CH)_{eq}$ is as high as 22·4 c/s. The magnitude of the axial/equatorial difference in all these compounds is appropriate to a chair rather than a boat conformation. Some support to our assignment of the 4,6 protons is provided by the values of $J(PO—O—CH)_{eq}$ = 20 c/s and $J(PS—O—CH)_{eq}$ = 19 c/s observed in comparable sterically rigid systems.[6]

Coupling constants J(P—O—CH) to the (presumably) freely rotating R_3 group, are quite close to the values within the ring, $J(P—O—CH)_{ax}$ and $J(P—O—CH)_{eq}$: J = 11·0 and 13·9 c/s in spectra 2·1 and 2·7. The apparent J(P—O—C*H*Me_2) in spectrum 2·3 (6·5 c/s) is surprisingly low.

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