Preparation and Properties of 1-Bromo-2,2,3,4,4-pentamethylphosphetan 1-Oxide, $C_8H_{16}P(O)Br$, and a Comparison with the Chloro-compound; Hydrolysis of These to the Anhydride and Acid. Vibrational Spectra

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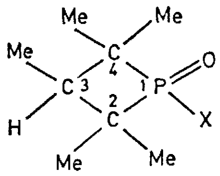
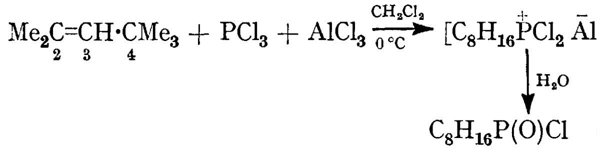
The title compound can be prepared from the reaction of 2,4,4-trimethylpent-2-ene, phosphorus tribromide, and aluminium bromide in dibromomethane followed by controlled hydrolysis. The inclusion of material containing chlorine results in the production of the well known 1-chloro-analogue, $C_8H_{16}P(O)Cl$. The bromo-derivative has been fully characterized and its reactivity towards common nucleophilic reagents shows it to be more reactive than the chloro-compound. At room temperature both undergo slow hydrolysis to the corresponding acid, $C_8H_{16}P(O)$-OH, whereas at higher temperatures the initial product is the anhydride, $C_8H_{16}P(O)\cdot O\cdot P(O)C_8H_{16}$. This compound is relatively resistant to further hydrolysis except by solution of pH >12. Kinetic studies show that hydrolysis under these conditions is of the first order in both anhydride and OH^-. Other ways of preparing the anhydride as well as its reactions have been studied. Raman and i.r. spectra of the bromide, chloride, acid, and anhydride are analysed; $\nu_s(POP)$ is identified.

THE parent compound of most phosphetan chemistry is 1-chloro-2,2,3,4,4-pentamethylphosphetan 1-oxide, $C_8H_{16}P(O)Cl$ (Ia). This is easily prepared[1] by reaction



X = Cl (Ia)
X = Br (Ib)
X = OH (Ic)
H—C (3) *trans* to P=O

(1) which gives *ca.* 80% of the phosphetan product, composed exclusively of the *trans*-isomer, the ring proton, C(3)–H, being *trans* to the phosphoryl group. A mechanism for the ring formation has been suggested which



$$\underset{2\;\;3\;\;4}{Me_2C{=}CH{\cdot}CMe_3} + PCl_3 + AlCl_3 \xrightarrow[0\,°C]{CH_2Cl_2} [C_8H_{16}\overset{+}{P}Cl_2\,\overset{-}{Al}Cl_4] \xrightarrow{H_2O} C_8H_{16}P(O)Cl \quad (1)$$

explains the migration of a methyl group from the 4- to the 3-position. The stereospecificity of the hydrolysis step remains a mystery. The original discoverers[1] of $C_8H_{16}P(O)Cl$ reported that it could be converted into the corresponding acid $C_8H_{16}P(O)OH$, the ^1H n.m.r. spectrum of which was used to deduce the cyclic structure of these compounds. They also reported that the pK_a of the acid was 2·85 and that it could be reconverted into the chloride by thionyl chloride. Since the original work on the acid little has been done on the hydrolysis of (Ia). Work by Bergesen[2] in which he converted (Ia) into the ethoxide, $C_8H_{16}P(O)OEt$, and then hydrolysed it to give the *cis*-acid leaving the *trans*-ester unaffected, remains unsubstantiated. It is highly unlikely in view of the high pK_a that *cis*- and *trans*-acids can be differentiated. *cis*- and *trans*-Isomers of several derivatives are known, in some cases being prepared as a mixture from the acid *via* regeneration of the chloride.[3]

Nucleophilic substitution of (I) proceeds *via* a penta-co-ordinate intermediate in which the phosphetan ring occupies an equatorial-apical posture, being constrained to this position by the ring bond angle at phosphorus which is $<90°$. Pseudorotation then manoeuvres the more electronegative, or apicophilic, group, which is the leaving group, into the apical position from which it can then depart. The result is retention of configuration at phosphorus in all cases.[4] This mechanism is purported to explain the substitution reactions of the phosphetans quantitatively,[5] the order of apicophilicity for the groups being assumed to be $N > Cl > O$.

It was hoped that the preparation of the bromo-derivative and a study of its nucleophilic substitutions would throw light on both these aspects of phosphetan chemistry. In particular, bromine being much less electronegative than chlorine should be less apicophilic. The first step is formation, by apical nucleophilic attack at P, of the five-co-ordinate intermediate requiring the halogen atom to be equatorial. This is more favourable for Br than Cl and the bromide should react faster. The second step is pseudorotation which is more favourable for Cl than Br and the chloride should react faster. The relative rates should decide which step is rate determining.

As well as comparing the reactivities of (Ib) and (Ia) towards amines and alcohols we have particularly chosen to study the hydrolysis of these compounds. This was prompted by the discovery of an unknown stable by-product which arose from several different reactions of the chloride.[6-8] This compound proved difficult to

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[1] J. J. McBride, jun., E. Jungermann ,J. V. Killheffer, and R. J. Clutter, *J. Org. Chem.*, 1962, **27**, 1833.

[2] K. Bergesen, *Acta Chem. Scand.*, 1967, **21**, 1587.

[3] S. E. Cremer and B. C. Trivedi, *J. Amer. Chem. Soc.*, 1969, **91**, 7200.

[4] J. R. Corfield, R. K. Oram, D. J. H. Smith, and S. Trippett, *J.C.S. Perkin I*, 1972, 713.

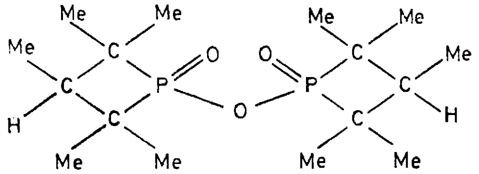
[5] J. R. Corfield, N. J. De'ath, and S. Trippett, *Chem. Comm.*, 1970, 1502.

[6] R. E. Ardrey, J. Emsley, A. J. B. Robertson, and J. K. Williams, *J.C.S. Dalton*, 1973, 2641.

[7] J. Emsley and J. K. Williams, *J.C.S. Dalton*, 1973, 1576.

[8] M. F. Crook, J. Emsley, T. B. Middleton, and J. K. Williams, *Phosphorus*, 1973, **3**, 45.

analyse but was eventually shown to be the anhydride (II). It is surprisingly stable for a compound with a P–O–P linkage. In view of the prodigious effort put



(II)

$C_8H_{16}P(O){\cdot}O{\cdot}P(O)C_8H_{16}$

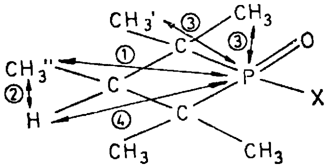
into the chemistry of the phosphetans in the past six years it is curious that this compound has so far escaped notice. As will be seen it could easily be mistaken for other compounds.

EXPERIMENTAL

Instruments.—N.m.r. spectra were recorded on Perkin-Elmer R12B (60 MHz) and Bruker HFX 90 (90 MHz, ^{1}H; 36·43 MHz, ^{31}P) spectrometers, the latter with Fourier and decoupling attachments. Compounds were studied in CCl_4 and $CDCl_3$ solutions and referenced to tetramethylsilane (^{1}H) and 85% H_3PO_4 (^{31}P). I.r. spectra were measured on a Perkin-Elmer 621 instrument with CsBr optics. Compounds were studied as Nujol and hexachlorobuta-1,3-diene mulls and the charts aligned against the polystyrene peak at 1601 cm^{-1}. Raman spectra were measured on a Cary 81 spectrometer by use of Kr 5682 Å laser emission line. Compounds were studied as liquids and chloroform solutions. Mass spectra were recorded on an A.E.I. MS-30 spectrometer operating with electron beam energy 24 eV; samples were introduced as *ca.* 50% (w/w) solutions in chloroform *via* a g.l.c. Carbowax column (200—210 °C).

TABLE 1

N.m.r. data



1 = ^4J(PCCCH$_3''$) X = Br (Ib)
2 = ^3J(HCCH$_3''$) X = Cl (Ia)
3 = ^3J(PCCH$_3$) X = OP(O)C_8H_{16} (II)
4 = ^3J(PCCH) X = OH (Ic)

	δ(CH$_3''$)*	^4J(PCCCH$_3''$)†	^3J(HCCH$_3''$)	δ(CH$_3$)*	^3J(PCCH$_3$)	δ(CH$_3'$)*	^3J(PCCH$_3'$)	δ(H)*	^3J(PCCH)	δ(OH)	δ(P)‡	^2J(POP)
(Ib)	0·97	1·52	7·43	1·37	23·81	1·38	21·32	1·73	7·68	—	86·14	—
(Ia)	0·95	1·76	7·28	1·36	23·53	1·39	21·71	1·80	3·84	—	80·74	—
(II)	0·95	0·88	7·08	1·31	20·24	1·34	20·08	1·69	6·60	—	57·37	18·64
(Ic)	0·89	1·82	7·44	1·20	17·54	1·24	17·52	1·66	6·80	12·75	57·56	—

* P.p.m. from tetramethylsilane. † Hz; error ± 0·05 Hz. ‡ P.p.m. from 85% H_3PO_4.

Preparation of 1-*Bromo*-2,2,3,4,4-*pentamethylphosphetan* 1-*Oxide from* 2,4,4-*Trimethylpent*-2-*ene*.—2,4,4-Trimethylpent-2-ene (56 g, 0·5 mol) was slowly added during 15 min to a well stirred mixture of phosphorus tribromide (135·4 g, 0·5 mol) and anhydrous aluminium bromide (133·3 g, 0·5 mol) in distilled dibromomethane (700 g) at 0 °C, and the mixture stirred for a further 90 min with the temperature kept below 10 °C. Water (300 cm^3) was added and the temperature kept below 35 °C. The red organic layer was separated, washed twice with water (50 cm^3), dried (Na_2SO_4), and the solvent stripped on a rotary evaporator. An almost colourless oil (107 g) was left which crystallized on standing. Recrystallization from light petroleum (b.p. 80—100 °C) gave 1-*bromo*-2,2,3,4,4-*pentamethylphosphetan* 1-*oxide* (70·2 g, 59%), m.p. 76—78 °C (Found: C, 40·4; H, 6·9; Br, 33·7; P, 12·9%; *m/e* 238. Calc. for $C_8H_{16}BrOP$: C, 40·15, H, 6·70; Br, 33·45; P, 12·95%; *M*, 238). ^{31}P N.m.r. is a complex multiplet (>11 peaks) details of which are in Table 1. The mass spectrum has been discussed.[6]

Preparation of 1-*Bromo*-2,2,3,4,4-*pentamethylphosphetan* 1-*Oxide from* 1-N-[1-*amino*-3-(*dimethylamino*)*propane*]-2,2,3,4,4-*pentamethylphosphetan* 1-*Oxide*.—The preparation of 1-*N*-[1-amino-3-(dimethylamino)propane]-2,2,3,4,4-pentamethylphosphetan 1-oxide, $C_8H_{16}P(O)NH{\cdot}(CH_2)_3{\cdot}NMe_2$, under atmospheric pressure conditions has been described.[7] This compound (2·60 g, 0·01 mol) was dissolved in light petroleum (30 cm^3, b.p. 80—100 °C) and saturated with dry hydrogen bromide (from bromine and tetrahydronaphthalene [9]). After 4 h at room temperature the precipitated amine dihydrobromide was filtered off and the solvent removed to give a quantitative yield of 1-bromo-2,2,3,4,4-pentamethylphosphetan 1-oxide (2·4 g, 0·01 mol), m.p. 76—78 °C after recrystallization from light petroleum. This compound is identical with that prepared above and since it must be the *trans*-isomer we can conclude that the above is also. The mechanism for the preparation of $C_8H_{16}P(O)Br$ and $C_8H_{16}P(O)Cl$ are presumably identical. This contrasts with the preparation of 1-phenyl-2,2,3,4,4-pentamethylphosphetan 1-oxide, $C_8H_{16}P(O)Ph$, from phenylphosphorus dichloride which gave a *cis*- and *trans*-mixture of isomers.[10]

Reaction of 2,4,4-*Trimethylpent*-2-*ene with* PX_3 *and* AlX_3 *in* CH_2X_2 (X = Cl *or* Br).—There are eight possible combinations of PCl_3 or PBr_3 with $AlCl_3$ or $AlBr_3$ in CH_2Cl_2 or CH_2Br_2 as solvent. One of these, in which all are chlorides, is the original reaction [1] for the preparation of (Ia). Another, in which all are bromides, is the reaction given above for the preparation of (Ib). In analogous reaction conditions the remaining six combinations were carried out. In every case the product was the chloro-derivative in excellent yields (see Table 2 which also contains the other two preparations for comparison). The combination of PBr_3 and $AlBr_3$ in CH_2Cl_2 was expected to produce $C_8H_{16}P(O)Br$

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[9] D. R. Duncan, *Inorg. Synth.*, 1939, **1**, 151.

[10] S. E. Cremer and R. J. Chorvat, *J. Org. Chem.*, 1967, **32**, 4066.

(this being our first attempt to prepare the bromo-derivative) but analysis of the *product* showed it to be $C_8H_{16}P(O)Cl$ (Found: C, 48·4; H, 8·0; Cl, 18·1; P, 16·7. Calc. for $C_8H_{16}ClOP$: C, 49·35; H, 8·3; Cl, 18·2; P, 15·9%). The ^{31}P n.m.r. spectrum of the product showed an impurity whose signals corresponded to those of the bromo-compound, but this constituted <10% of the total yield.

TABLE 2

Reaction of 2,4,4-trimethylpent-2-ene with PX_3 and AlX_3 in CH_2X_2. The product in all cases except the last was $C_8H_{16}P(O)Cl$, and in the last was $C_8H_{16}P(O)Br$

Molar scale	Reactants PX_3	AlX_3	Solvent	Yield (%)
0·5	PCl_3	$AlCl_3$	CH_2Cl_2	77
0·1	PCl_3	$AlCl_3$	CH_2Br_2	65
0·1	PCl_3	$AlBr_3$	CH_2Cl_2	69
0·1	PCl_3	$AlBr_3$	CH_2Br_2	68
0·5	PBr_3	$AlCl_3$	CH_2Cl_2	68
0·1	PBr_3	$AlCl_3$	CH_2Br_2	62
0·1	PBr_3	$AlBr_3$	CH_2Cl_2	74*
0·5	PBr_3	$AlBr_3$	CH_2Br_2	59

* Contains *ca.* 10% $C_8H_{16}P(O)Br$.

Reaction of 1-*Bromo*-2,2,3,4,4-*pentamethylphosphetan* 1-*Oxide with Diethylamine.*—1-Bromo-2,2,3,4,4-pentamethylphosphetan 1-oxide (11·9 g, 0·05 mol), diethylamine (3·7 g, 0·05 mol), and triethylamine (5·1 g, 0·05 mol) were refluxed in toluene (150 cm³) for 14 h under dry oxygen-free nitrogen. ^1H N.m.r. showed that only 6% of 1-(*NN*-diethylamino)-2,2,3,4,4-pentamethylphosphetan 1-oxide had been formed. A similar experiment with the chloride, $C_8H_{16}P(O)Cl$, and diethylamine gave only 2% product.

Reaction of $C_8H_{16}P(O)Br$ *with* NN-*Dimethylaminopropane*-1,3-*diamine.*—1-Bromo-2,2,3,4,4-pentamethylphosphetan 1-oxide (2·4 g, 0·01 mol), *NN*-dimethylaminopropane-1,3-diamine (1·02 g, 0·01 mol), and triethylamine (1·01 g, 0·01 mol) were refluxed in toluene (60 cm³) under dry oxygen-free nitrogen for 25 min [equation (2)]. A similar reaction with $C_8H_{16}P(O)Cl$ (1·94 g, 0·01 mol) was carried out simultaneously. The reaction mixtures were quickly cooled, filtered to remove the triethylamine hydrohalides, and the solvents stripped *in vacuo*. ^1H N.m.r. showed that 1-*N*-[1-amino-3-(dimethylamino)propane]-2,2,3,4,4-pentamethylphosphetan 1-oxide had formed in yields of 31 and 14% from (Ib) and (Ia) respectively. $C_8H_{16}P(O)Cl$ forms a quantitative yield of $C_8H_{16}P(O)NH{\cdot}(CH_2)_3{\cdot}NMe_2$ after refluxing with $NH_2{\cdot}(CH_2)_3{\cdot}NMe_2$ in toluene for 3 h.[7]

$$C_8H_{16}P(O)Br + H_2N(CH_2)_3NMe_2 \longrightarrow HBr + C_8H_{16}P(O)NH(CH_2)_3NMe_2 \quad (2)$$

Reaction of $C_8H_{16}P(O)Br$ *with Methanol.*—1-Bromo-2,2,3,4,4-pentamethylphosphetan 1-oxide (11·9 g, 0·05 mol), methanol (1·6 g, 0·05 mol), and triethylamine (5·1 g, 0·05 mol) were refluxed in toluene (100 cm³) for 4 h under dry oxygen-free nitrogen. The yield of 1-methoxy-2,2,3,4,4-pentamethylphosphetan 1-oxide was 7·5 g, 79%. By comparison the yield from the same reaction with $C_8H_{16}P(O)Cl$ was 7·0 g (74%).

Hydrolysis of $C_8H_{16}P(O)Br$ *and* $C_8H_{16}P(O)Cl$.—When samples ($2{\cdot}5 \times 10^{-4}$ mol) of the solid halides were exposed to the air they picked up water and were slowly hydrolysed to the acid $C_8H_{16}P(O)OH$. Hydrolysis after 1 day was 22% for $C_8H_{16}P(O)Cl$ and 44% for $C_8H_{16}P(O)Br$; after 2 days 57 and 79%; and after 3 days 68 and 87% respectively. In another series of experiments samples ($2{\cdot}5 \times 10^{-4}$ mol) of the halides were dissolved in $(CD_3)_2CO$ (0·5 cm³) and water (0·045 g, $2{\cdot}5 \times 10^{-4}$ mol) added. The products of hydrolysis at 25 °C were a mixture of the acid $C_8H_{16}P(O)OH$ and the anhydride $C_8H_{16}P(O){\cdot}O{\cdot}P(O)C_8H_{16}$, as shown by ^1H n.m.r. studies. Hydrolysis after 1 day was 45% for $C_8H_{16}P(O)Cl$ and 72% for $C_8H_{16}P(O)Br$; after 2 days 79 and 95%; and after 3 days 85 and >99%, respectively.

Hydrolysis of $C_8H_{16}P(O)Cl$ *at Higher Temperatures.*—*Formation of the anhydride.* The phosphetan anhydride first appeared when the chloride was refluxed with methanol in the presence of triethylamine. Unsuspected traces of water picked up by the chloride were responsible. In a series of runs $C_8H_{16}P(O)Cl$ (11·4 g, 0·059 mol), triethylamine (6·0 g, 0·059 mol), and water (0·5 g, 0·028 mol) in 1,4-dioxan (150 cm³) were heated on a water-bath for 2 h. The yields of anhydride at various temperatures were 36% at 51·0 °C; 42% at 61·3 °C; 47% at 71·0 °C; 53% at 77·3 °C; and 61% at 95·0 °C. The *anhydride*, $C_8H_{16}P(O){\cdot}O{\cdot}P(O)C_8H_{16}$, is a white, air-stable, crystalline solid, m.p. 150—151 °C [Found: C, 57·5; H, 9·6; P, 18·4%; *M* (cryoscopic in benzene), 337 ± 5. Calc. for $C_{16}H_{32}O_3P$: C, 57·5; H, 9·65; P, 18·5%; *M*, 334]. Elemental analysis of the anhydride by three independent laboratories invariably gave low results for phosphorus. Only by taking extra precautions, *e.g.*, very slow combustion, were correct values obtained by the National Physical Laboratory. ^1H N.m.r. spectra of the anhydride seemed to indicate the presence of a small amount of a second isomer. However, samples of the anhydride were submitted for g.l.c.–mass spectral analysis and showed only one isomer even when this had been formed from the acid by reaction with thionyl chloride. On one occasion two isomers were observed in the anhydride produced in the reaction of $C_8H_{16}P(O)Cl$ and $Pb(SEt)_2$[6] but separated by such long retention times that it seems likely that a column reaction was responsible. (As pointed out by a Referee, these may be rotational isomers.) T.l.c. studies also showed that the anhydride was composed of only one isomer.

Reaction of $C_8H_{16}P(O)Cl$ *and* $C_8H_{16}P(O)OH$.—The chloride (9·8 g, 0·05 mol) and the acid (8·8 g, 0·05 mol) were refluxed in toluene (50 cm³) for 2 h although evolution of hydrogen chloride from the mixture died away rapidly after 15 min. The yield of anhydride (16·7 g, 0·05 mol) was 51% m.p., 148—151 °C after recrystallization from light petroleum (b.p. 60—80 °C). In the presence of triethylamine the yield of anhydride was only 41%.

Reaction of $C_8H_{16}P(O)OH$ *and* $SOCl_2$.—The acid (17·6 g, 0·10 mol) and thionyl chloride (6·0 g, 0·05 mol) were refluxed in toluene (150 cm³) for 2 h to give a 48% yield of the anhydride.

Reaction of the Anhydride with Nucleophilic Reagents.—The anhydride is stable for >7 days in water at room temperature; at 100 °C it is converted into the acid; 35% conversion after 1 h. The anhydride reacts very slowly with methanol and diethylamine under reflux conditions in toluene and not at all at room temperature. Sodium chloride in refluxing MeCN gave no reaction. The anhydride reacts rapidly with sodium hydroxide solution to give the sodium salt of the acid.

Reaction of the Anhydride with Hydrogen Bromide.—A solution of the anhydride (3·3 g, 0·01 mol) in light petroleum (b.p. 40—60 °C) was saturated with dry hydrogen bromide and left at room temperature for 3 h, after which the solvent was stripped *in vacuo*. The residue was then dissolved in dichloromethane, washed several times with distilled water, and dried (Na_2SO_4), and the solvent removed *in vacuo*. ^1H N.m.r. showed that a mixture of acid and (Ib) had formed [equation (3)]. When the experiment was repeated with

$$\mathrm{C_8H_{16}P(O){\cdot}O{\cdot}P(O)C_8H_{16} + HBr \longrightarrow C_8H_{16}P(O)Br + C_8H_{16}P(O)OH} \quad (3)$$

dry hydrogen chloride under the same conditions the anhydride was recovered unaffected.

Kinetic Studies of the Hydrolysis of the Anhydride by NaOH.—A standard aqueous solution of the anhydride was mixed with a standard solution of sodium hydroxide at 25 °C. At time *t* a 10 cm^3 aliquot portion was removed and added to 10 cm^3 of standard hydrochloric acid solution, thereby quenching the reaction. Back titration gave the extent of reaction. By this method initial rates were obtained for varying concentration of anhydride and OH^- (Table 3).

TABLE 3

Hydrolysis of $C_8H_{16}P(O){\cdot}O{\cdot}P(O)C_8H_{16}$ by NaOH solution

[Anhydride] / mmol/10^3 cm^3	[NaOH] / mmol/1000 cm^3	Initial rate / µmol anhydride (10^3 cm^3)$^{-1}$ min^{-1}
0·50	4·0	2·66
1·00	4·0	4·03
1·50	4·0	9·70
2·00	4·0	14·8
2·50	4·0	15·9
3·00	4·0	21·0
3·00	6·0	11·4
3·00	12·0	14·1
3·00	24·0	30·0
3·00	36·0	42·0
3·00	72·0	87·0

Plots of log (initial rates) against log [OH] and against log [anhydride] gave straight-line graphs of slopes 0·92 and 1·04 respectively showing the hydrolysis to be of the first order in both anhydride and hydroxide. The average rate constant for the reaction was $1{\cdot}72 \times 10^{-2}$ l mol^{-1} s^{-1}.

Attempted Preparation of 1-*Iodo*-2,2,3,4,4-*pentamethylphosphetan* 1-*Oxide*.—No $C_8H_{16}P(O)I$ was formed when solutions of the amide $C_8H_{16}P(O)NEt_2$ were saturated with anhydrous hydrogen iodide prepared from refluxing a solution of iodide in tetrahydronaphthalene.[11] That a reaction had occurred was evident from the complexity of the ^1H n.m.r. spectrum of the solution but no product was isolated.

DISCUSSION

The phosphetan bromide, $C_8H_{16}P(O)Br$, has been prepared by two methods summarized as (4) and (5). Scheme (4) is a modified form of the reaction of the benzylamino-derivative, $C_8H_{16}P(O)NHCH_2Ph$, and

$$\begin{tikzcd} \underset{trans}{\mathrm{C_8H_{16}P(O)Cl}} \arrow[r, "\mathrm{NH_2{\cdot}(CH_2)_3{\cdot}NMe_2}"] & \underset{trans}{\mathrm{C_8H_{16}P(O)NH{\cdot}(CH_2)_3{\cdot}NMe_2}} \arrow[d, "\mathrm{HBr}"] \\ & \underset{trans}{\mathrm{C_8H_{16}P(O)Br}} \end{tikzcd} \quad (4)$$

hydrogen chloride which Trippett reported to give high yields of $C_8H_{16}P(O)Cl$,[12] with retention of configuration. We have used the *NN*-dimethylpropane-1,3-diamino-derivative since this is the easiest amino-compound to prepare,[7] and from it obtained excellent yields of $C_8H_{16}P(O)Br$ which it is assumed will be the *trans*-isomer. Attempts to use this method to prepare $C_8H_{16}P(O)I$ did not succeed.

Method (5) produces exactly the same isomer as shown by its ^1H n.m.r. spectrum. This scheme is analogous to that originally discovered for preparing $C_8H_{16}P(O)Cl$ even

$$\begin{tikzcd} \mathrm{Me_2C{=}CH{\cdot}CMe_3 + PBr_3 + AlBr_3} \arrow[r, "\mathrm{CH_2Br_2}"] & {[\mathrm{C_8H_{16}\overset{+}{P}Br_2\ \overset{-}{Al}Br_4}]} \arrow[d, "\mathrm{H_2O}"] \\ & \mathrm{C_8H_{16}P(O)Br} \end{tikzcd} \quad (5)$$

down to its being stereospecific in favour of the *trans*-isomer. The yield of the bromo-compound is 59% which is lower than for the chloro (77%) but this difference can in part be accounted for by the greater ease of hydrolysis of the former than of the latter. The yield also seems dependent on the solvent used as Table 2 shows: when CH_2Cl_2 is replaced by CH_2Br_2 in the reaction involving PCl_3 and $AlCl_3$ (first two reactions on the list) there is a drop in yield of *ca.* 10%. Also when $AlBr_3$ replaces $AlCl_3$, as in the first and third reactions on the list, there is also a drop in yield.

It is not surprising that the reaction of 2,4,4-trimethylpent-2-ene with PCl_3 gives only the chloro-derivative, $C_8H_{16}P(O)Cl$, when the 'catalyst' is either $AlCl_3$ or $AlBr_3$ and the solvent is either CH_2Cl_2 or CH_2Br_2 or combinations of these. What is surprising is that the corresponding reaction of the olefin with PBr_3 will only yield the desired bromophosphetan $C_8H_{16}P(O)Br$ when both catalyst and solvent are $AlBr_3$ and CH_2Br_2. If either is the chloride then the product is $C_8H_{16}P(O)Cl$. A solution of $C_8H_{16}P(O)Br$ in CH_2Cl_2 does not produce $C_8H_{16}P(O)Cl$, nor does $AlBr_3$ in CH_2Cl_2 produce $AlCl_3$. Therefore, in the penultimate reaction in Table 2, the mechanism whereby the chlorine of the solvent ends up in the product suggests that the role of the solvent in this reaction is more complex than hitherto thought. The equilibrium (6) could explain the redistribution of a

$$\mathrm{PX_3 + RX + AlX_3 \rightleftharpoons [RPX_3]^+[AlX_4]^-} \quad (6)$$

particular halogen between the solvent RX and the catalyst AlX_3.[13] Reaction (7) then explains how the

$$\mathrm{PX_3 + AlY_3 \longrightarrow PY_3 + AlX_3} \quad (7)$$

halogen with the stronger P–X bond finds its way into the product. Thus any chlorine in the system will turn up in the product in preference to bromine. The overall reaction (1) is more complex than previously assumed.

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[11] C. J. Hoffman and E. A. Heintz, *Inorg. Synth.*, 1963, **7**, 180.

[12] K. Ellis, D. J. H. Smith, and S. Trippett, *J.C.S. Perkin I*, 1972, 1184.

[13] J. I. Bullock, N. J. Taylor, and F. W. Parret, *J.C.S. Dalton*, 1972, 1843 and refs. 1—8 therein.

The bromophosphetan $C_8H_{16}P(O)Br$ reacts with diethylamine, methanol, and water in the same way as the chlorophosphetan to give the same products but faster in all cases. The rate-determining step would therefore seem to be the initial attack, which should be faster for the bromide than the chloride, rather than the pseudorotation step which is favoured by the chloride.

Hydrolysis.—At 25 °C hydrolysis proceeds slowly and directly (8). When performed in an organic solvent or

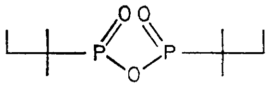
$$C_8H_{16}P(O)(Cl,Br) + H_2O \longrightarrow C_8H_{16}P(O)OH + HCl,HBr \quad (8)$$

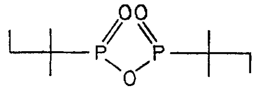
at higher temperatures a secondary reaction (9) becomes

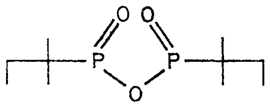
$$C_8H_{16}P(O)(Cl,Br) + C_8H_{16}P(O)OH \longrightarrow C_8H_{16}P(O)OP(O)C_8H_{16} + HCl,HBr \quad (9)$$

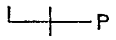
important. Presumably, under these conditions the acid, or its conjugate base anion, is a stronger nucleophile towards $C_8H_{16}P(O)Cl$ than water.

The Anhydride.—Unlike other P–O–P compounds, and phosphinic anhydrides in particular,[14,15] this phosphetan anhydride is fairly resistant to nucleophilic attack. Its appearance as a by-product in reactions designed to prepare alkoxides from ROH and amines from RNH_2 and R_2NH attests to its stability.[7,8] Its production in these reactions was due to water impurity. It is stable in water and a measurable rate of hydrolysis at 25 °C only occurs when the pH exceeds *ca.* 12. A closer study of this reaction shows it to be of the first order in the anhydride and in OH^-, and the rate constant is $1{\cdot}72 \times 10^{-4}$ l mol^{-1} s^{-1}. The relative stability of the anhydride is presumably due to a combination of steric factors [16-18] and relative apicophilicities [5] with the former predominating, but the latter is important in the reactions with HX. The anhydride is readily cleaved by HBr but not by HCl. This observation can be explained in terms of the five-co-ordinate intermediate model if the apicophilicities of the groups is Cl > $OP(O)C_8H_{16}$ > Br.

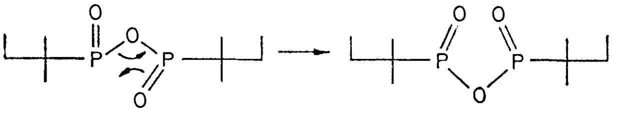

trans-trans
(III)


trans-cis
(IV)

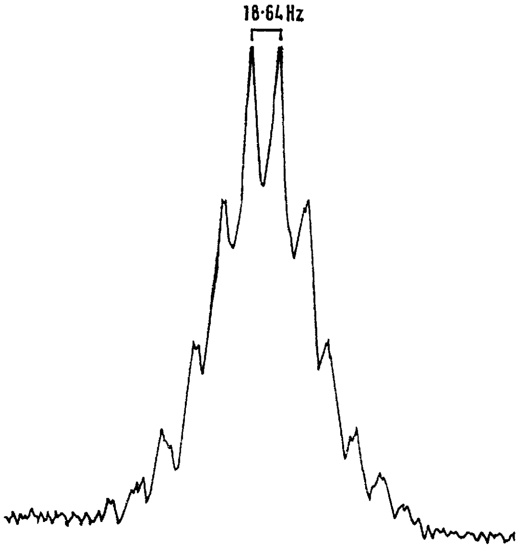

cis-cis
(V)


= side view of ring

The anhydride consists predominantly of one isomer as shown by g.l.c.–mass spectrometry and t.l.c. Three isomers are in theory possible, shown diagramatically as (III)—(V). If the source of one of the rings is the acid or its anion (both of which exist as a mixture of isomers) then the product should be a mixture of isomers. That only one isomer is found suggests either (i) a stereospecific reaction in the formation of the anhydride or (ii) a rearrangement of one of the isomers to the other more stable isomer. An intramolecular rearrangement leads to interisomer conversion, *e.g.*, (10). Which isomer is the stable one is not known.


trans-cis *trans-trans*
(10)

The n.m.r. spectra of phosphetans are usually of the first order and these compounds are no exception; shifts and coupling constants are in Table 1. ^{31}P Decoupling was used to confirm assignments. The anhydride has the ^{31}P n.m.r. spectrum shown in the Figure which at first glance seems to show the phosphorus coupled to an odd number of identical neighbours. The spectrum is explained as a pair of almost coincident overlapping multiplets. This is due to the coupling between the two phosphorus atoms [^2J(POP) 18·64 Hz] being nearly the same as that between a phosphorus and the methyl protons of the α-carbon of its phosphetan ring [^3J(PCMe) 20·16 Hz].



^{31}P N.m.r. spectrum of $C_8H_{16}P(O){\cdot}O{\cdot}P(O)C_8H_{16}$

Vibrational Spectra.—In a previous paper [7] the i.r. spectra of several amine derivatives of (Ia) were reported and several bands picked out as characteristic of the

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TABLE 4

Vibrational spectra (cm^{-1})

$C_8H_{16}P(O)Br$	$C_8H_{16}P(O)Cl$		$C_8H_{16}P(O)OH$		$C_8H_{16}P(O){\cdot}O{\cdot}P(O)C_8H_{16}$		$C_8H_{16}PO_2Na$	
I.r.	I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.	Assignments
						130w,dp		
		153m,dp		190w,dp		155w,dp		
				218m,–				
				245w,–				
				325s,dp	338w	330m,p	325w	
335w	344m	346vs,p	357w	348m,–				
			368w	378s,–			377m	
395w	398w		398w		408w	400vw,–	405w	Phosphetan
408w			420s	424w		427vw,–	415w	
			432m	438s	438s	435vw,–	440w	
450sh	458w	457s,p						
478s								ν(P–Br)
490s	493m		498m	500vw	500vw	500w,p		
501s	508s		515sh					
	518s	513s,p *						ν(P–Cl)
523m	525sh		525s	526w,p	524s		530sh	Phosphetan
					533s		543ms	and/or PO_2
559w	556w	558s,p	551w	556s,p	558m	558vs,p	560vw	Phosphetan
					600m	611s,p		ν_s(POP)
626m	641vs	637m,p	626m	630vs,p	630s	625ssh,p	633m	Phosphetan
			634m	641vs,p				
654w	662s	664w,–	677s	680w,–	670s	677w,p	655sh	Phosphetan
					677s		668	
						720w,–		
750m	752s	758w,–	750m	757m,–	754m	758m,–	753w	Phosphetan
890sh	890w				895sh			
900w					905sh			
915sh								
928w	932m	943w,dp	933s	941m,br	929s		928m	Phosphetan
					951m	952mbr,dp		ν_{as}(POP)
			955sbr	958m,dp				ν_t(O–H–O)
985w	997w		992m					
1016w	1020m	1021vs,dp	1019m	1020vs,dp	1021w	1021vw,dp	1012ms	
							1031s	$\nu_s(PO_2^-)$
1049w	1050m	1052vw,dp	1050s	1050vw,dp	1050w	1050w,dp	1047s	$\rho(CH_3)$
1070w	1074m	1079vw,?	1070s	1075vw,?	1076w	1078w,dp	1079s	Phosphetan ?
			1100s,vbr	1100w,p				ν_b(O–H–O)
	1109w	1112vw,dp				1112vw,dp		
	1125w	1125vw,dp		1130w,p		1127vw,dp		
1150sh							1147vs	$\nu_{as}(PO_2^-)$
							1160s	
1164m	1167s	1170w,dp			1171w	1172w,p		
	1195sh		1180sbr					
1209m	1216vs	1211m–	1205sh	1200vw,–	1212s	1217w,p		ν(P=O)
1248m	1257vs	1254w,dp	1242s	1242vw,–	1260s	1260w,dp	1229m	Phosphetan
1256sh					1265s			ν_{as}(CPC)
	1274m							
1330w	1333vw	1339vs,–		1340w,p	1341w	1341vw,–		
1370m	1375w		1373w		1371m		1360m	$\delta_s(CH_3)$
1382w	1385w		1385w		1385m		1385m	
1393w	1396w	1400vw,p	1394w	1397w,p	1395m	1397w,p		
1435sh	1432sh							
1448sh	1459vs	1443m,dp	1453m	1445m,dp	1437m	1443m,dp		$\delta_{as}(CH_3)$
1462s	1463vs	1460w,dp	1459m	1457w,–	1455s		1452mbr	
1470sh	1469vs	1483w,–	1469m	1468m,p?	1468s	1467m,dp		
			1635sbr					1205 + 432
			2250sbr					1100 + 1180
			2600sbr					ν_s(O–H–O)
2860s	2865m	2870m,p	2870s	2870s,p	2865s	2868s	2860s	$\nu_{s,as}(CH_3)$
2900sh	2900sh	2918m,p	2900sh		2900sh	2919vs,p	2900s	
2930s	2925s	2934s,p	2920sh	2935vs,p	2930s	2936vs,p	2950vs	
2960sh	2965sh		2960vs	296ts,p			2965vs	
2980s	2975vs	2975m,dp	2980sh	2980w,dp	2970s	2970s,dp		

* For solid; 529s,p CCl_4 solution.

phosphetan ring. A band in the 1200—1300 cm^{-1} region was amongst these but a definite assignment was impossible because of the proximity to the ν(P=O) band. To clear up this and other assignments, *e.g.*, the P–O–P modes, both the i.r. (250—4000 cm^{-1}) and Raman (100—3000 cm^{-1}) spectra of the chloride, anhydride, and acid are given in Table 4 which also includes the i.r. spectra of the bromide and the salt $C_8H_{16}P(O)ONa$. The methyl vibrations are the most intense but fall within regions which are not occupied by other vibrations.

The phosphetan bands are found at 1242—1265, 925—933, 750—754, 662—677, 627—641, 550—558, 500—525 (doublet with shoulders), and 398—400 cm^{-1}. Some of these are weak in the i.r. but appear as strong polarized Raman bands. The highest band can now with certainty be identified with ν_{as}(C–P–C) since it is depolarized whereas ν(P=O) falls at 1180—1217 cm^{-1} and is polarized as required (anhydride spectra). Its sensitivity to substitution at phosphorus accounts for its variation in location, and the same would probably be true of ν_s(C–P–C). On these grounds the bands at 627—641 cm^{-1} can be singled out and they are also polarized but the 500—525 cm^{-1} is a more likely contender. The i.r. spectrum of $C_8H_{16}P(O)ONa$ seems decisive in that it gives sharper peaks for the phosphetan vibrations in several regions and especially at 543, 928, and 1229 cm^{-1}. The first is higher than in any other derivative so far encountered and the last is lower confirming these peaks' susceptibilities to change at phosphorus. In this salt the PO_2^- bands are a very strong pair at 1147 and 1031 cm^{-1}.

The anhydride spectra are currently the most interesting in view of the ' controversy ' over ν_s(P–O–P). It is now generally agreed that ν_{as}(P–O–P) falls at *ca.* 950 cm^{-1} [19] although even in the recently published spectra of $F_2P(O)OP(O)F_2$ and its sulphur analogues it is put at 1050 cm^{-1} in preference to this region.[20] In more recent work on $(CF_3)_2P(S){\cdot}O{\cdot}P(S)(CF_3)_2$ it is assigned to a triplet at 929 cm^{-1}.[21] The band at 951 cm^{-1} in $C_8H_{16}P(O){\cdot}O{\cdot}P(O)C_8H_{16}$ which is Raman-depolarized clearly fits ν_{as}(P–O–P). Its symmetric counterpart has no generally recognized spectral region but in this case the strong polarized mode at 611 cm^{-1} is the only possible assignment for ν_s(P–O–P). The i.r. band at 600 cm^{-1} may be its counterpart.

Compounds containing the P(O)OH group are characterized by five broad bands [22] which are found in the acid at 2600, 2250, 1635, 955, and 500 cm^{-1}. These are designated in terms of the strong H-bonding expected in this compound [23] or as combination bands. A study of the i.r. spectrum of the acid in 0·4—0·001M concentrations in carbon tetrachloride failed to show any change in ν_s(O–H · · · O) or the appearance of an acid monomer peak at *ca.* 3500 cm^{-1}. This difference between P(O)OH and C(O)OH systems has been attributed to much stronger H-bonding in the former.[24] However, in the study of the H-bonding between $C_8H_{16}P(O)OEt$ and phenol in carbon tetrachloride Aksnes and Albriktsen [25] conclude that the small Δν(OH) of 310 cm^{-1} observed for this pair is evidence of weaker H-bonding which is inhibited by steric effects of the four α-methyl groups. The obvious conclusion is *intra*molecular H-bonding for $C_8H_{16}P(O)OH$, but as this was once claimed for other phosphinic acids and later shown to be invalid,[26] doubt must remain.

In the chloride and bromide the region 400—525 cm^{-1} is very complex. Both have strong bands centred on 508 and 501 cm^{-1} respectively (with accompanying shoulders and sub-peaks in the region 490—525 cm^{-1}) and these are assigned to ν_s(C–P–C). In the chloride there is a strong peak at 518 cm^{-1} which is assigned to ν(P–Cl); Chittenden and Thomas give the range 521—523 cm^{-1} based on only three $R_2P(O)Cl$ derivatives.[27] The ν(P–Br) mode presents some difficulty; only two bands qualify for this, 408w or 478s cm^{-1}. The latter seems the more likely, in that its presence in the spectrum is otherwise unassignable, and yet it seems rather high for this vibration.

We thank J. S. Elliott, B. T. Davis, G. J. J. Jayne, and M. F. Crook for discussion, the Burmah Oil Trading Co. Ltd. for a grant, and the S.R.C. for awards (to T. B. M. and J. K. W.).

[3/979 *Received*, 14*th May*, 1973]

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