Investigations into the Reaction of Phosphorus Trihalides and Alkenes and the Formation of the Phosphetan Ring

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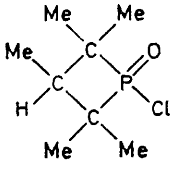
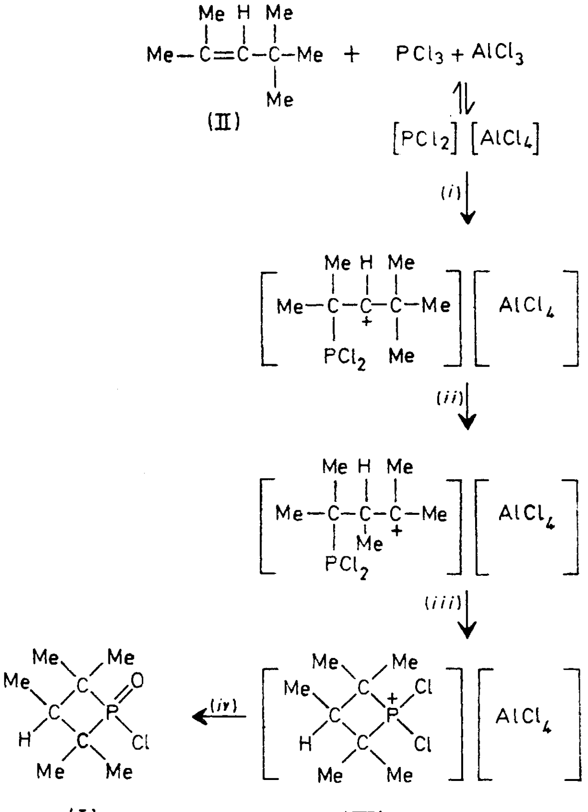
A fresh look has been taken at the reaction of phosphorus trihalides and alkenes in the presence of the corresponding aluminium trihalide which yields phosphetans in high yield. The reaction can give rise to several by-products, especially if equimolar ratios of the reactants are not adhered to. The by-products have been investigated and their formation explained. The hydrolysis step of the reaction is stereospecific in some instances but not in others, and the preparation of 1-chloro-2,2,3-trimethylphosphetan 1-oxide has been used to probe this aspect of the reaction. Attempts to form phosphazene links involving phosphetans have been unsuccessful. The compound 1-amino-2,2,3,4,4-pentamethylphosphetan 1-oxide is reported.

THE chemistry of phosphetans, which are four-membered heterocyclic phosphorus compounds, was given a boost in 1962 by the publication of a simple recipe for preparing them.[1] The original paper was devoted to the formation and characterisation of 1-chloro-2,2,3,4,4-pentamethylphosphetan 1-oxide, $C_8H_{16}PClO$ (I), which is formed in yields of *ca.* 80% by the addition of 2,4,4-trimethylpent-2-ene, (II), to a cooled solution of PCl_3 and $AlCl_3$ in CH_2Cl_2 and then by treating the resulting mixture with ice-cold water.[1] Other workers have since extended the reaction to other alkenes and/or $PMeCl_2$,[2,3] $PPhCl_2$,[2-4] or PBr_3.[5] Cremer and his co-workers have isolated some of the ionic intermediates such as $[C_8H_{16}PMeCl][AlCl_4]$ and $[C_8H_{16}PPhCl][AlCl_4]$, thus confirming the mechanism proposed by the original discoverers and shown in Scheme 1. However, it was as a result of unexpected difficulties experienced in the preparation[5] of 1-bromo-2,2,3,4,4-pentamethylphosphetan 1-oxide, $C_8H_{16}PBrO$, that a closer look at the general reaction seemed timely.



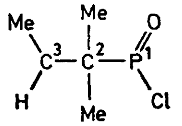
(I)

Most research on the phosphetans has been with the original 2,2,3,4,4-pentamethylphosphetan system. One reason for remaining with this is that the reaction for the preparation of $C_8H_{16}PClO$ gives a product consisting purely of the *trans* isomer. [The earlier workers thought they had produced a mixture of *cis* and *trans* isomers but it was later shown that the product was solely *trans*.[6]] The definition of *trans* in this molecule is with respect to the proton on C^3 being *trans* to the phosphoryl oxygen in that they are on opposite sides of the ring as the side view illustrated in (IV). Sometimes mixtures of *cis* and *trans* compounds are produced as in the preparation of $C_8H_{16}PRCl^+$ (R = Me, Ph, and Bu^t) from alkene and $PRCl_2$.[3] Cremer studied the interconversion of these isomers, noting that when the corresponding anion was $[AlCl_4]^-$ there was no interconversion, but when it was Cl^- then interconversion occurred. This was interpreted as evidence for a five-co-ordinate intermediate C_8H_{16}-$PRCl_2$. No one has yet considered the effect of changes



(I) (III)

SCHEME 1 (*i*), CH_2Cl_2; (*ii*), methyl migration; (*iii*), ring closure; (*iv*), H_2O



(IV)

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[3] S. E. Cremer, F. L. Weitl, F. R. Farr, P. W. Kremer, G. A. Gray, and H-O. Hwang, *J. Org. Chem.*, 1973, **38**, 3199.

[4] S. E. Fishwick and J. A. Flint, *Chem. Comm.*, 1968, 182.

[5] J. Emsley, T. B. Middleton, and J. K. Williams, *J.C.S. Dalton*, 1973, 2701.

[6] Mazhar-ul-Haque, *J. Chem. Soc.* (*B*), 1970, 934.

in the ring moiety in so far as these affect the product isomer distribution. However, the use of a less-substituted ring can add to our knowledge as we shall see. The work reported in this paper deals mainly with the non-phosphetan by-products of the reaction and how these are affected by changes in the conditions.

EXPERIMENTAL

Instruments.—N.m.r. spectra were recorded on Brucker HFX90 (90 MHz, ^{1}H; 36.42 MHz, ^{31}P) and Perkin-Elmer R12B (60 MHz) instruments, the former with Fourier and decoupling attachments. Compounds were referenced to SiMe$_4$ (^{1}H) and 85% H$_3$PO$_4$ (^{31}P). Molecular weights were determined on samples dissolved in CHCl$_3$ using a Perkin-Elmer–Hitachi (model 115) molecular-weight apparatus. I.r. spectra were recorded on a Perkin-Elmer 621 instrument with CsBr optics and the charts were aligned against the polystyrene peak at 1 601 cm^{-1}. Mass spectra (*m/e* values) were obtained *via* a g.l.c. attachment to an A.E.I. MS30 spectrometer.

Variations in the Preparation of C$_8$H$_{16}$PClO.—(i) AlCl$_3$. The amount of AlCl$_3$ was varied from zero to the equimolar amount used in the original reaction [1] and beyond. In a typical reaction, 2,4,4-trimethylpent-2-ene (56.0 g, 0.5 mol) was slowly added to a mixture of PCl$_3$ (68.7 g, 0.5 mol) and AlCl$_3$ (0—99 g, 0—0.625 mol) in CH$_2$Cl$_2$ (300 cm^3) at 0 °C. After stirring for 1 h, water (400 cm^3) was added until two layers formed and the organic layer was separated, dried, stripped of solvent, and the products investigated. With no AlCl$_3$, no phosphetan was produced; instead a mixture was obtained of 2-chloro-2,4,4-trimethylpentane, Me$_2$C(Cl)-CH$_2$CMe$_3$ (Found: C, 64.8; H, 11.5; Cl, 23.4%; *m/e* 148. Calc. for C$_8$H$_{17}$Cl: C, 64.8; H, 11.4; Cl, 23.6%, *M* 148), n_D^{20} 1.4302 (lit.,[7] 1.4308), ^{1}H n.m.r. δ 1.05 (s, 9 H), 1.66 (s, 6 H), and 1.87 (s, 2 H), 1-chloro-2,4,4-trimethylpent-2-ene, ClCH$_2$C(Me):CHCMe$_3$ (Found: C, 65.5; H, 9.9; Cl, 24.4%; *m/e* 146. Calc. for C$_8$H$_{15}$Cl: C, 65.5; H, 10.2; Cl, 24.4%; *M* 146), n_D^{20} 1.4472 (lit.,[8] 1.4468), δ 1.04 (s, 9 H), 1.85 (d, 3 H, *J* 1 Hz), 4.18 (s, 1 H), and 4.91 p.p.m. (m, 2 H), and t-butylphosphonic dichloride, PBu^{t}Cl$_2$O, m.p. 122 °C (lit.,[9] 123 °C) (Found: C, 27.2; H, 5.0; Cl, 39.9; P, 17.5%; *m/e* 174. Calc. for C$_4$H$_9$Cl$_2$OP: C, 27.4; H, 5.1; Cl, 40.6; P, 17.5%; *M* 174), δ 1.40 p.p.m. [d, 9 H, *J*(HCCP) 25 Hz, as reported [10]]. Trace amounts of 2,4,4-trimethylpent-1-ene were also produced in the reaction. The ratio of the three major components was 1 : 1 : 0.3 respectively and they were separated by fractional distillation. Of these, PBu^{t}Cl$_2$O has a characteristic camphor-like odour and the smell of this by-product can sometimes be detected in the normal reaction. 2-Chloro-2,4,4-trimethylpentane must have been produced before the addition of water to the reaction. This was demonstrated by the fact that the reaction between the alkene and hydrogen chloride gives a quantitative yield of this compound under anhydrous conditions but none is formed if water is present.

When AlCl$_3$ is used in the reaction C$_8$H$_{16}$PClO is produced although the amount is always less than the amount of AlCl$_3$ employed. For instance, when the ratio of alkene : PCl$_3$: AlCl$_3$ was 1 : 1 : 0.75 then the yield of C$_8$H$_{16}$PClO was *ca.* 50%. For a 1 : 1 : 1 ratio, the yield of phosphetan increased to *ca.* 80%, while an excess of AlCl$_3$ in a 1 : 1 : 1.25 ratio of reactants gave a product which was >95% phosphetan. With a deficit of PCl$_3$, some of the alkene was converted into higher polymers, exclusively so when no PCl$_3$ was present. As the amount of PCl$_3$ decreased in proportion to the alkene, so the yield of phosphetan product decreased.

(ii) *Other Lewis-acid chlorides*. (a) *Iron*(III) *chloride*. 2,4,4-Trimethylpent-2-ene (11.2 g, 0.1 mol) was added over a period of 15 min to a well stirred mixture of PCl$_3$ (13.8 g, 0.1 mol) and anhydrous FeCl$_3$ (16.2 g, 0.1 mol) in CH$_2$Cl$_2$ (80 cm^3) at 0 °C. After stirring for 1 h, water was slowly added until two layers formed. The CH$_2$Cl$_2$ layer was separated, dried, stripped of solvent, and the products investigated. These were found to be a mixture of polymerised alkenes of which the dimer, C$_{16}$H$_{32}$, was separated by fractional distillation and identified (Found: C, 85.5; H, 14.0%; *M* 217. C$_{16}$H$_{32}$ requires C, 86.8; H, 14.2%; *M* 224). The undistilled residue analysed as C, 85.4; H, 14.0%, which showed it to be C$_n$H$_{2n}$ and with *M* 562 corresponding to alkene pentamer (*M* 560), C$_{40}$H$_{80}$, although this is certainly a mixture of higher and lower polymers whose average molecular weight is very close to that of the pentamer. There was no evidence of phosphetan formation, nor of any of the chlorinated hydrocarbon by-products.

(b) *Zinc chloride*. A reaction on the scale, and by the method, described for FeCl$_3$ gave a 1 : 0.8 ratio of 1-chloro-2,4,4-trimethylpent-2-ene and 2-chloro-2,4,4-trimethylpentane, analogous to the reaction of 2,4,4-trimethylpent-2-ene and PCl$_3$ in the absence of AlCl$_3$.

(iii) *The solvent*. When CH$_2$Cl$_2$ was replaced by a purely aliphatic hydrocarbon solvent (hexane) or a purely aromatic hydrocarbon solvent (toluene) in the reaction of 2,4,4-trimethylpent-2-ene, PCl$_3$, and AlCl$_3$, no phosphetan was formed. Instead alkene dimer was formed in each case. When another chlorinated hydrocarbon solvent was used such as 1,2-dichloroethane, a 3 : 2 ratio of phosphetan, C$_8$H$_{16}$PClO, to alkene dimer, C$_{16}$H$_{32}$, resulted. A similar mixture of products was observed when 1,2-dibromoethane was used in place of CH$_2$Br$_2$ in the reaction of 2,4,4-trimethylpent-2-ene, PBr$_3$, and AlBr$_3$ which gave an 11 : 9 ratio of C$_8$H$_{16}$PBrO : C$_{16}$H$_{32}$.

(iv) *Alkenes*. The use of 2,4,4-trimethylpent-1-ene, CH$_2$=C(Me)CH$_2$CMe$_3$, in place of the corresponding pent-2-ene gave no phosphetan product. Instead a mixture consisting of 22% PBu^{t}Cl$_2$O, 38% alkene dimer, C$_{16}$H$_{32}$, and 40% of an undistillable mixture with an empirical composition C$_{33}$H$_{66}$ClO$_3$P$_3$ was obtained. The by-product from some of the reactions described above was 1-chloro-2,4,4-trimethylpent-2-ene which should be a suitable alkene for phosphetan formation. However, no phosphetan product resulted when this reacted with PCl$_3$ and AlCl$_3$, only a polymerised alkene appeared to have been formed.

Preparation of 1-*Chloro*-2,2,3-*trimethylphosphetan* 1-*Oxide*.—3,3-Dimethylbut-1-ene (42 g, 0.5 mol) was added over a period of 10 min to a well stirred mixture of PCl$_3$ (68.8 g, 0.5 mol) and anhydrous AlCl$_3$ (66.6 g, 0.5 mol) in dry CH$_2$Cl$_2$ (300 cm^3) at 0 °C. After stirring for 1 h under dry N$_2$, water was added (300 cm^3) and the organic layer was separated, dried, and stripped of solvent on a rotary evaporator to yield a mixture, as shown by the ^{1}H n.m.r. spectrum, of 16% cis- and 84% trans-1-*chloro*-2,2,3-*trimethylphosphetan* 1-*oxide* (77 g, 0.46 mol, 92%), m.p. 25—32 °C, which slowly

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[8] J. I. Jones, *J. Chem. Soc.*, 1957, 2735.

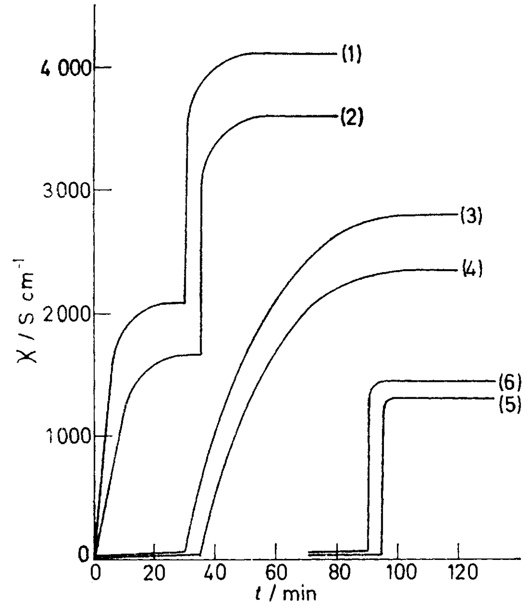
[9] J. P. Clay, *J. Org. Chem.*, 1951, **16**, 892.

[10] T. Siddall and C. A. Prohaska, *J. Amer. Chem. Soc.*, 1962, **84**, 2502.

crystallised in a refrigerator. Fractional crystallisation gave a sample of pure *trans* isomer, m.p. 38—40 °C (Found: C, 43.6; H, 7.20; Cl, 21.5; P, 18.5%; *m/e* 166. Calc. for $C_6H_{12}ClOP$: C, 43.2; H, 7.20; Cl, 21.3; P, 18.6%; *M* 166), δ 1.10 [dd, 3 H, $J(H_3CCH)$ 7], 1.37 [d, 3 H, $J(PCCH_3)$ 24], 1.38 [d, 3 H, $J(PCCH_3)$ 25 Hz], and 1.74—3.14 p.p.m. (m, 3 H, protons attached to ring carbons).

Hydrolysis of the chloride gave the phosphetan acid,[11] $C_6H_{12}PO(OH)$, m.p. 48—51 °C, *m/e* 148 (*M* 148), δ 1.05 [dd, 3 H, $J(H_3CCH)$ 7], 1.17 [d, 3 H, $J(PCCH_3)$ 20], 1.28 [d, 3 H, $J(PCCH_3)$ 21 Hz], 1.57—3.4 (m, 3 H, protons attached to ring carbons), and *ca.* 12.5 p.p.m. (br s, 1 H, OH).

trans-1-*Ethylthio*-2,2,3-*trimethylphosphetan* 1-*Oxide*.—This was prepared by the sodium ethanethiolate method [12] which gave a yield of 52% of trans-1-*ethylthio*-2,2,3-*trimethylphosphetan* 1-*oxide*, b.p. 90—91 °C (0.5 mmHg),* *m/e* 192 (*M* 192), δ 1.10 [dd, 3 *H*, $J(H_3CCH)$ 7], 1.26 [d, 3 H, $J(PCCH_3)$ 21], 1.35 [d, 3 H, $J(PCCH_3)$ 18], 1.39 [t, 3 H, SCH_2CH_3, $J(PSCCH_3)$ 8], 1.60—3.20 (partly hidden by SCH_2 peaks, m, 3 H, protons attached to ring carbons), and 2.96 p.p.m. [dq, 2 H, SCH_2, $J(PSCH_2)$ 8 Hz].



Conductance studies on reactions of alkenes, PX_3, and AlX_3 in the formation of $[C_nH_{2n}PX_2][AlX_4]$. The numbers refer to equations in the text

Conductance Measurements.—Phosphorus halide (0.05 mol) and aluminium halide (0.05 mol) were added to the corresponding dihalogenomethane (200 cm³) in a flask equipped with a conductivity cell and flushed with oxygen-free dry N_2. The mixture was stirred until all, or as much as possible, of the aluminium halide had dissolved as shown by the conductance of the solution remaining steady with time. The alkene (0.05 mol) was then added in a single step and changes in the conductance of the solution were observed. The results are shown in the Figure. The solutions were dilute enough to dissipate the heat of reaction and a temperature rise of only 2—3 °C was observed. This affected the conductance only marginally. Six reactions were followed in this manner, three with each of the alkenes 2,4,4-trimethylpent-2-ene, C_8H_{16}, and 3,3-dimethylbut-1-ene, C_6H_{12}. The reactions studied are those of equations (1)—(6) and these numbers correspond to the plots in the Figure. The ¹H n.m.r. spectrum of the phosphetanium

$$C_8H_{16} + PPhCl_2 + AlCl_3 \xrightarrow{CH_2Cl_2} [C_8H_{16}PPhCl][AlCl_4] \quad (1)$$

$$C_6H_{12} + PPhCl_2 + AlCl_3 \xrightarrow{CH_2Cl_2} [C_6H_{12}PPhCl][AlCl_4] \quad (2)$$

$$C_8H_{16} + PCl_3 + AlCl_3 \xrightarrow{CH_2Cl_2} [C_8H_{16}PCl_2][AlCl_4] \quad (3)$$

$$C_6H_{12} + PCl_3 + AlCl_3 \xrightarrow{CH_2Cl_2} [C_6H_{12}PCl_2][AlCl_4] \quad (4)$$

$$C_8H_{16} + PBr_3 + AlBr_3 \xrightarrow{CH_2Br_2} [C_8H_{16}PBr_2][AlBr_4] \quad (5)$$

$$C_6H_{12} + PBr_3 + AlBr_3 \xrightarrow{CH_2Br_2} [C_6H_{12}PBr_2][AlBr_4] \quad (6)$$

product of reaction (1) has been reported,[3] those for (3) and (4) were impossible to obtain because a suitable solvent could not be found, and those for (2), (5), and (6) are listed in the Table.

Reactions of 1,1-*Dichloro*-2,2,3,4,4-*pentamethylphosphetanium Tetrachloroaluminate*.—This compound, the product of equation (3), and the compound most commonly prepared as the intermediate to $C_8H_{12}PClO$, was studied in greater detail. It is a pale green crystalline compound which turns pink at 127 °C, white at 220 °C, but does not melt below 300 °C. When stored in a sealed ampoule it is stable for several months. It is insoluble in $CHCl_3$, CCl_4, C_6H_6, and alkanes. It undergoes solvolysis with OEt_2 and dimethyl sulphoxide (dmso).

(i) *With water*. When the salt is exposed to the air it becomes crimson in *ca.* 3 h and evolves HCl. The addition of water is usually performed *in situ* as part of the general reaction whence the product is *trans*-$C_8H_{16}PClO$. The same reaction occurs when water and the solid salt react and is exothermic. The product does not vary whether the salt is added to a large volume of ice and water and the temperature remains at 0 °C or whether water is added dropwise to the salt and the temperature allowed to rise unchecked.

¹H N.m.r. spectra of the protons of the phosphetanium ring cations

Compound	C^3CH_3 (dd)		C^2CH_3 (d)		C^2CH_3 (d)		C^3H (m
	δ [a]	$J(HCCH_3)$ [b]	δ	$J(PPCH_3)$	δ	$J(PCCH_3)$	δ
$[C_8H_{16}PBr_2][AlBr_4]$	1.67	7.0	2.12	35.0	2.16	34.0	3.44
$[C_6H_{12}PBr_2][AlBr_4]$	1.46	7.0	1.76	35.0	1.78	34.0	2.90—4.50 [c]
$[C_6H_{12}PPhCl][AlCl_4]$	1.08	7.0	1.41	28.1	1.46	25.3	3.05—4.10 [c]

[a] In p.p.m. with respect to $SiMe_4$. [b] In Hz. [c] All three protons attached to the ring carbons are coupled and produce a complex set of signals.

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

[11] J. I. G. Cadogan, D. T. Eastlick, J. A. Challis, and A. Cooper, *J.C.S. Perkin II*, 1973, 1798.

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

No *cis* isomer was detected in either case. Among the by-products of hydrolysis there were always small amounts of the phosphetan acid, $C_8H_{16}PO(OH)$, and the anhydride, $C_8H_{16}P(O)O(O)PC_8H_{16}$.[13]

(*ii*) *With* H_2S. Attempts to prepare 1-chloro-2,2,3,4,4-pentamethylphosphetan 1-sulphide by treating the salt with H_2S gave only a 2% yield of this, identified by g.l.c. and mass spectrometry.

(*iii*) *With* $[NH_4]Cl$. The salt (45 g, 0.118 mol) and $[NH_4]Cl$ (12.6 g, 0.236 mol) were heated in refluxing tetrachloroethane (500 cm^3) for 16 h. Removal of the solvent however gave a black tarry mass, the ^1H n.m.r. spectrum of which showed no identifiable phosphetan resonances, and consequently no attempt was made to separate the mixture.

1-*Amino*-2,2,3,4,4-*pentamethylphosphetan* 1-*oxide*. 1-Chloro-2,2,3,4,4-pentamethylphosphetan 1-oxide (3 g, 0.015 mol) and liquid NH_3 (30 cm^3) were left in contact at −78 °C for 48 h and the mixture was stirred occasionally. Unchanged NH_3 was allowed to evaporate and the resulting white solid was extracted with light petroleum (b.p. 60—80 °C) which removed unchanged chloride. Treatment of the residue with $CHCl_3$ caused the product, 1-*amino*-2,2,3,4,4-*pentamethylphosphetan* 1-*oxide*, $C_8H_{16}P(NH_2)O$ (1.5 g, 0.008 mol, 55% yield), which was soluble, to separate from the $[NH_4]Cl$. The product crystallised as fine white needles, m.p. 149—151 °C [Found: C, 55.0; H, 10.1; N, 8.00; P, 17.6. Calc. for $C_8H_{18}NOP$: C, 54.9; H, 10.3; N, 8.00; P, 17.7%), δ 0.89 [dd, 3 H, $J(H_3CCH)$ 8], 1.19 [d, 6 H, $J(PCCH_3)$ 17], 1.24 [d, 6 H, $J(PCCH_3)$ 18 Hz], 1.72 (dq, 1 H), and *ca.* 3.15 p.p.m. (br m, 2 H, NH_2). The last peak was sensitive to concentration and varied within the range 2.95—3.35 p.p.m., suggestive of intermolecular rather than intramolecular hydrogen bonding. In the presence of D_2O this resonance disappeared, identifying the protons as those of the NH_2 group.

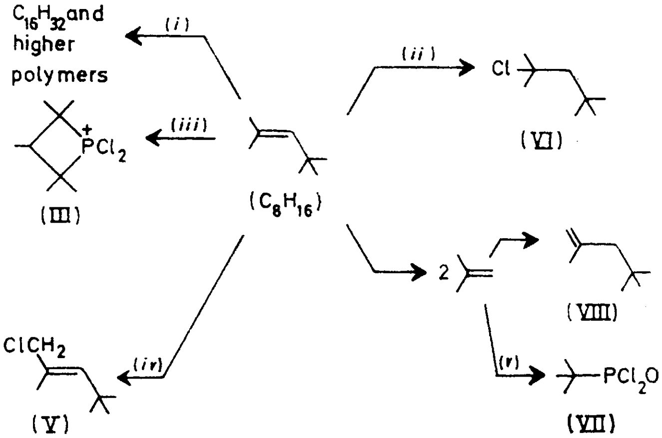
The products of the reaction of $C_8H_{16}P(NH_2)O$ and PCl_5 were submitted to g.l.c.–mass spectrometry but none of the desired $C_8H_{16}P(NPCl_3)O$ was observed. No attempt was made to investigate further the products of this reaction.

Reaction of 1-*Chloro- and* 1-*Amino*-2,2,3,4,4-*pentamethylphosphetan* 1-*Oxides*.—The compound $C_8H_{16}PClO$ (2.33 g, 0.012 mol), $C_8H_{16}P(NH_2)O$ (1.75 g, 0.01 mol), NEt_3 (1.01 g, 0.01 mol), and toluene (20 cm^3) were degassed and sealed in a thick-walled glass tube *in vacuo*. The mixture was heated for 16 h at 220 °C. The product was filtered off and separated from $[NEt_3H]Cl$ with light petroleum (b.p. 60—80 °C). Evaporation of this solvent gave an oil which failed to crystallise even after standing at 0 °C for 1 month. This *product* was $C_8H_{16}P(O)NH(O)PC_8H_{16}$ (2.6 g, 0.0078 mol, 78%) (Found: C, 57.7; H, 10.2; N, 4.45; P, 18.1%; *m/e* 333. Calc. for $C_{16}H_{33}NO_2P$: C, 57.7; H, 9.9; N, 4.20; P, 18.6%; *M* 333).

DISCUSSION

The reaction of 2,4,4-trimethylpent-2-ene or 3,3-dimethylbut-1-ene and PCl_3 or PBr_3 in the presence of the corresponding aluminium halide goes much more rapidly than hitherto expected, as revealed by the changes in conductance (Figure). The bromide studies are the most revealing since the original adduct, $AlBr_3 \cdot PBr_3$, is completely soluble and un-ionised while the phosphetanium intermediates are also completely soluble and ionised. The jumps in conductance shown in plots (5) and (6) coincide with the addition of the alkene to the solution, and indicate the rapidity of the formation of the phosphetan ring system. But this is not the only unusual feature of this reaction which our investigations have uncovered.

The original workers[1] stipulated an equimolar ratio of the reactants alkene, PCl_3, and $AlCl_3$. Adherence to this ratio is important in controlling the amount of by-products of the reaction. Most of these have been identified and their proportions in the final mixture increases if the criterion of equimolar amounts of reactants is not complied with. The by-products and the conditions which facilitate their formation are in Scheme 2. The ratio of $PCl_3 : AlCl_3$ was varied over the whole range from 0 : 1 to 1 : 0. In the absence of $AlCl_3$, 2,4,4-trimethylpent-2-ene reacts with PCl_3 to form 1-chloro-2,4,4-trimethylpent-2-ene, (V), by substituting one of the ethylenic methyl protons. The hydrogen chloride produced by this reaction can then add across the double bond of another alkene molecule to give 2-chloro-2,4,4-trimethylpentane, (VI). Formation of (V) may take place by an autoinitiated radical mechanism *via* peroxides formed by absorption of O_2 from the air.[14]



SCHEME 2 (*i*), $AlCl_3$ in excess; (*ii*), HCl from step (*iv*); (*iii*), $AlCl_3$, and PCl_3 in correct ratio; (*iv*), PCl_3, in excess; (*v*), PCl_3 and H_2O

The presence of a strong Lewis acid such as $AlCl_3$ suppresses the substitution (and hence the subsequent addition) and as the ratio of $AlCl_3$ increases so does the yield of desired phosphetan. A weak Lewis acid such as $ZnCl_2$ however fails in this respect and substitution still occurs. With a 1 : 1 ratio of $PCl_3 : AlCl_3$, or preferably a slight excess of $AlCl_3$, phosphetan is the dominant product. With an excess of $AlCl_3$ over PCl_3, polymerisation of the olefin competes with phosphetan formation. If a very strong Lewis acid such as $FeCl_3$ is used in place of $AlCl_3$ then the polymerisation is paramount and no phosphetan forms.

The production of t-butylphosphonic dichloride, (VII),

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

[14] P. Sykes, 'A Guide Book to Mechanism in Organic Chemistry,' 3rd edn., Longmans, London, 1970, p. 268.

is not easily rationalised but may result from depolymerisation of the alkene into isobutene, a process which is known to occur in the presence of PCl_3.[15] This may then react as in sequence (7). The production of small

$$Me_2C{=}CH_2 \xrightarrow{H^+} [Bu^t]^+ \xrightarrow{PCl_3} PBu^tCl_3{}^+ \xrightarrow{H_2O} PBu^tCl_2O + HCl + H^+ \quad (7)$$

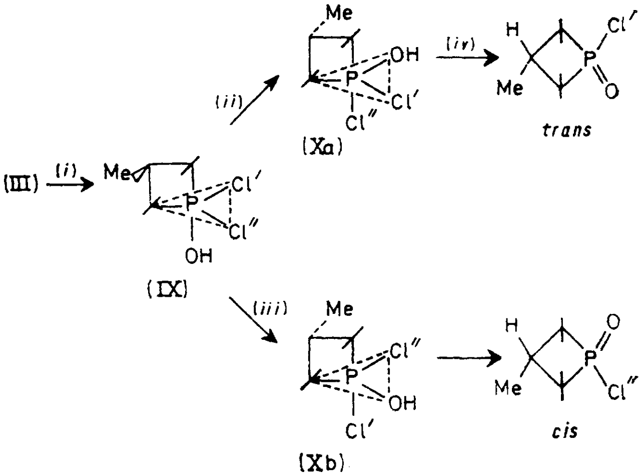
amounts of 2,4,4-trimethylpent-1-ene would support this dissociation of the pent-2-ene to isobutene.

Although the choice of solvent is important [5] and the control of the temperature is less important than previously assumed, the suitability of the alkene is the primary factor in the reaction. The earlier workers tried a range of olefins without obtaining phosphetan derivatives.[16] To their list we can now add 2,4,4-trimethylpent-1-ene and 1-chloro-2,4,4-trimethylpent-2-ene. The reaction with 3,3-dimethylbut-1-ene does give 2,2,3-trimethylphosphetans. Derivatives of this ring are known, such as $C_6H_{12}PPhO$,[2] $C_6H_{12}PO(OMe)$,[17] $C_6H_{12}PO(OH)$,[11] and $C_6H_{12}P(O)C(:NOH)C_6H_4NO_2$-*p*,[11] and these were formed *via* the 1-chloro-compound $C_6H_{12}PClO$ although this has never been separated and characterised as such. In fact the hydrolysis step in the reaction of 3,3-dimethylbut-1-ene, PCl_3, and $AlCl_3$ does not produce exclusively the *trans* isomer, as it does in the case of $C_8H_{16}PClO$, but gives a mixture of *cis* and *trans* with the latter predominating. The *trans* isomer can be separated by fractional crystallisation and a derivative $C_6H_{12}PO(SEt)$ has been made.

The Hydrolysis Step.—When the phosphetanium salt is treated with water the second part of the reaction occurs and the product is the phosphetan 1-oxide. There may be small amounts of the phosphetan acid and anhydride formed at this stage also. In the hydrolysis of 1,1-dichloro-2,2,3,4,4-pentamethylphosphetanium tetrachloroaluminate, (III), the product is exclusively the *trans* isomer, *trans*-$C_8H_{16}PClO$, which may come from the five-co-ordinate intermediate (IX) in Scheme 3. It can be deduced, since no *cis* isomer is formed, that the pseudorotation [(IX) ψ(Cl″) (Xb)] is energetically unfavourable. This situation we can ascribe to steric crowding in which the methyl group on the C^3 ring atom interacts with the chlorine atom in (Xb).

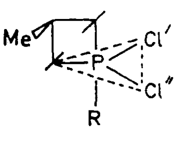
That the steric crowding of three methyl groups and a chlorine atom at one side of the phosphetan ring is the key to the stereospecificity is shown apparently by the hydrolysis of the 2,2,3-trimethylphosphetanium intermediate. In the five-co-ordinate arrangement postulated in the hydrolysis step the steric overcrowding is partially relieved by there being one methyl group less, so that the pseudorotations corresponding to step [(IX) ψ(Cl″) (Xb)] are possible with the result that some *cis* isomer of $C_6H_{12}PClO$ is formed.

Related to this problem is that of isomer interconversion of *cis*- and *trans*-phosphetanium derivatives. Cremer *et al.*[3] studied this in depth. They suggest that for interconversion to occur the trigonal-bipyramidal

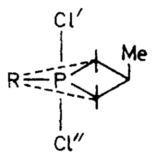


SCHEME 3 (*i*), OH⁻; (*ii*), ψ(Cl′); (*iii*), ψ(Cl″); (*iv*), −HCl

intermediate must adopt one of two energetically unfavourable configurations during pseudorotation, *i.e.* (XIa) or (XIb). In the former, ψ(Cl′) will give the *cis* isomer and ψ(Cl″) will give the *trans* isomer, *cis* and *trans* referring here to the C^3 methyl group and the group R. Configuration (XIa) however is unfavourable because it places R in an apical position. In (XIb) the



(XIa)



(XIb)

loss of Cl′ will produce the *cis* isomer, and the loss of Cl″ will produce the *trans* isomer; (XIb) is an unfavourable configuration because it places the ring diequatorial and thereby imposes strain on the ring bond angles.

Whichever the mechanism the surprising result was that isomer interconversion resulted in a preponderance of the *cis* isomer in the case of the phenyl and t-butyl compounds and the *trans* isomer with the methyl one. On steric grounds there can be no convincing explanation of these observations, and Cremer's results must cast a shadow on any reasoning which invokes *cis* interaction with the C^3 methyl group. Yet it is difficult to account for the exclusive formation of *trans*-$C_8H_{16}PClO$ without bringing in steric factors.

The intermediate $[C_8H_{16}PCl][AlCl_4]$ was heated with $[NH_4]Cl$ in the hope of forming a series of cyclopolyphosphazenes $(C_8H_{16}PN)_n$ ($n = 3$, 4, *etc.*) with a spiro arrangement of phosphetan and phosphazene rings at each phosphorus centre. Heating PCl_5 and PR_2Cl_3 compounds with $[NH_4]Cl$ leads to $(Cl_2PN)_n$ [18] and $(R_2PN)_n$

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[15] G. J. J. Jayne and J. S. Elliott, personal communication.

[16] E. Jungerman, J. J. McBride, jun., R. Clutter, and A. Mais, *J Org. Chem.*, 1962, **27**, 606.

[17] W. Hawes and S. Trippett, *Chem. Comm.*, 1968, 579.

[18] J. Emsley and P. B. Udy, *J. Chem. Soc.* (*A*), 1971, 768.

(R = Me, Et, *etc.*)[19] products respectively, and the mechanism involves $[PCl_4]^+$ and $[PR_2Cl_2]^+$. For this reason it was hoped that $[C_8H_{16}PCl_2]^+$ would behave similarly. Unfortunately no phosphetan compounds were produced. The synthesis of the amino-derivative $C_8H_{16}P(NH_2)O$ also offered the chance of forming phosphazene derivatives by reaction with PCl_5 to give $C_8H_{16}P(NPCl_3)O$ but again no identifiable product resulted.

The amino-derivative $C_8H_{16}P(NH_2)O$ is itself an interesting compound. Amides of dialkylphosphinic acids, $PR_2(NH_2)O$, cannot be purified by distillation as they eliminate NH_3 to form the imide [equation (8)[20,21]].

$$2PR_2(NH_2)O \longrightarrow R_2P(O)NH(O)PR_2 + NH_3 \quad (8)$$

However, $C_8H_{16}P(NH_2)O$ was distilled without such decomposition and attempts to synthesise the imide proved difficult and forcing conditions were needed (220 °C, 16 h), equation (9), which is rather surprising in view of the ease of formation of the isoelectronic phosphetan anhydride, $C_8H_{16}P(O)O(O)PC_8H_{16}$.[13]

$$C_8H_{16}P(NH_2)O + C_8H_{16}PClO \longrightarrow C_8H_{16}P(O)NH(O)PC_8H_{16} + HCl \quad (9)$$

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[20] O. A. Mukhacheva and A. I. Razumov, *Zhur. obshchei Khim.*, 1962, **32**, 2696.

[21] A. I. Razumov and N. G. Zabusova, *Zhur. obshchei Khim.*, 1962, **32**, 2688.