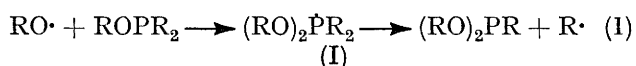


## Configurational Effects in the $\alpha$ -Scission of Phosphoranyl Radicals

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The rates of  $\alpha$ -scission of a series of dialkyldi-*t*-butoxyphosphoranyl radicals  $R^1R^2\dot{P}(OBu^t)_2$ , in which  $R^1$  and  $R^2$  may be the same or different, have been measured by kinetic e.s.r. spectroscopy. The results are rationalised in terms of  $\alpha$ -scission occurring faster when an apical rather than an equatorial P-C bond undergoes cleavage. It is suggested that the increase in rate of  $\alpha$ -scission along the series  $L_2\dot{P}(OBu^t)_2 < L_2\dot{P}(OBu^t)OEt < L_2\dot{P}(OEt)_2$  ( $L$  = alkyl or  $R_2N$ ) is due to the increased proportion of the isomer with an apical P-L bond which is present as the number of ethoxy-ligands increases. However, if configurational effects are absent, changing the nature of the alkoxy-substituents in a phosphoranyl radical has only a small effect on the rate of its  $\alpha$ -scission. The equatorial P-C bond dissociation enthalpy of  $Me\dot{P}(OPr^i)_3$  is found to be ca. +29 kJ mol<sup>-1</sup>. The radicals  $Me_3\dot{P}OR$  ( $R$  = Et, Bu<sup>t</sup>, *t*-pentyl) undergo exchange of apical and equatorial methyl groups on the e.s.r. time scale, and  $k_{exch} = 4 \times 10^6$  s<sup>-1</sup> for  $Me_3\dot{P}OBu^t$  at -70°. It is suggested that the low selectivity observed for the overall displacement of alkyl radicals from  $R^1R^2\dot{P}$  by *t*-butoxyl radicals may be due to the low selectivity of the phosphoranyl radical formation step, which is product controlling.

ALKOXYL radicals react with alkoxyalkylphosphines to displace an alkyl radical from phosphorus.<sup>1,2</sup> This  $S_N2$  reaction [equation (1)] proceeds by a stepwise mechanism involving  $\alpha$ -scission of a trigonal bipyramidal phosphoranyl radical intermediate (I).<sup>2</sup>



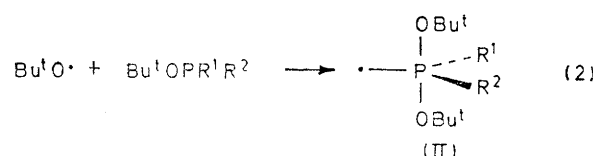
We have proposed that such  $\alpha$ -scission is a configurationally selective process in which an apical P-C bond is cleaved more rapidly than an equatorial P-C bond.<sup>2</sup> We now report results obtained with phosphoranyl radicals containing different *P*-alkyl groups, and other evidence, which strongly support this proposal.

### RESULTS AND DISCUSSION

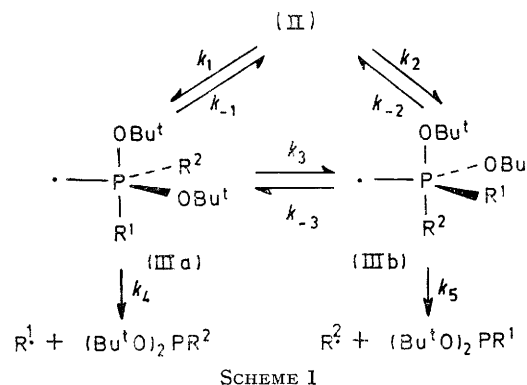
(a) *Generation and Detection by E.s.r. Spectroscopy of Phosphoranyl Radicals*.—Most of the phosphoranyl radicals studied in this work were produced by addition of photochemically-generated alkoxy radicals to alkoxyalkylphosphines using cyclopropane or propane as solvent.<sup>2</sup> Solutions containing diethyl or di-*t*-butyl peroxide and the phosphine were irradiated with high intensity u.v. light while the samples were in the cavity of an e.s.r. spectrometer. The decay kinetics of the phosphoranyl radicals could be measured by monitoring the intensity of their e.s.r. spectra as a function of time after interruption of photolysis, where necessary using a computer to average out instrumental noise associated with rapid decay.<sup>3</sup>

(b)  *$\alpha$ -Scission of Dialkyldi-*t*-butoxyphosphoranyl Radicals*.—The radicals  $R^1R^2\dot{P}(OBu^t)_2$  were generated by addition of *t*-butoxyl radicals to the dialkyl-*t*-butoxyphosphines,  $R^1R^2POBu^t$ , which were present in the system either as primary reagents or were produced by the reaction of *t*-butoxyl radicals with trialkylphosphines<sup>2</sup> (see below). The only isomer of these phosphoranyl radicals detect-

able by e.s.r. spectroscopy is (II), in which the alkyl groups are in equatorial ligand sites.<sup>2,4</sup>



The e.s.r. spectroscopic parameters and the observed first-order decay rate constants ( $k_{obs}$ ) for the species (II) are gathered in Table 1. It is clear that the kinetic results given in Table 1 are inconsistent with a direct fragmentation of (II) which occurs by cleavage of an equatorial P-C bond, since in such a case the rate constants should increase smoothly as the strength of the P-C bond decreases. The observed high stability of (II;  $R^1 = R^2 = Bu^t$ ) may be explained if decay of (II) occurs predominantly by way of an undetected less stable isomer (III) with an apical P-C bond which undergoes rapid homolysis.<sup>2</sup> Calculations<sup>5,6</sup> show that apical P-ligand



bonds in phosphoranyl radicals are longer (and presumably weaker) than the corresponding equatorial bonds to the same type of ligand.

In Scheme 1 phosphoranyl radical isomerisations are

<sup>5</sup> A. Hudson and J. T. Wiffen, *Chem. Phys. Letters*, **1974**, **29**, 113.

<sup>6</sup> A. J. Colussi, J. R. Morton, and K. F. Preston, *J. Phys. Chem.*, **1975**, **79**, 651.

<sup>1</sup> W. G. Bentrude, 'Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, New York, 1973, vol. 2, ch. 22.

<sup>2</sup> A. G. Davies, R. W. Dennis, and B. P. Roberts, *J.C.S. Perkin II*, **1974**, 1101.

<sup>3</sup> R. W. Dennis and B. P. Roberts, *J.C.S. Perkin II*, **1975**, 140.

<sup>4</sup> P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, **1972**, **94**, 6033.

shown as permutations of the type <sup>3,\*</sup> (1)(234). The alternative ligand permutation mode, represented, for instance, by (12)(3)(4) cannot be excluded for these radicals although it may be for others.<sup>3</sup>

The relative magnitudes of the rate constants for isomerisation and for fragmentation of (IIIa and b) are difficult to estimate accurately at present, but the observed decay rates of (II) can best be interpreted in terms of a situation in which  $k_{-1} > k_4$  and  $k_{-2} > k_5$ , when configurational isomers will be present in something

the alkyl radical increases, and hence the strength of the apical P-C bond in (III) decreases. For (II;  $R^1 = R^2 = \text{Bu}^t$ ), although  $k_4$  is presumably greater than for the di-isopropyl analogue,  $K_1$  is probably much smaller<sup>2</sup> because of an unfavourable steric interaction between the apical and equatorial t-butyl groups in (III).

The observed decay rate constants for the mixed alkylphosphoranyl radicals are consistent with these proposals. The radical (II;  $R^1 = \text{Bu}^t$ ,  $R^2 = \text{Me}$ ) decays extremely rapidly, the final products being  $\text{MeP}(\text{OBu}^t)_2$

TABLE 1  
Hyperfine coupling constants and decay rate constants for  $R^1R^2\dot{\text{P}}(\text{OBu}^t)_2$  in cyclopropane

Phosphoranyl radical (II)		Source	Hyperfine splitting <sup>a</sup> (G)		Temp. range (°C)	$k_{\text{obs}}/\text{s}^{-1}$ <sup>b,c</sup> (-100°)	$E_a^{\text{obs}}/\text{kJ mol}^{-1}$ <sup>b,c</sup>	$\log_{10} A^{\text{obs}}/\text{s}^{-1}$ <sup>b,c</sup>
$R^1$	$R^2$		a(P)	a(H)				
Me	Me	$\text{Me}_2\text{P}\dot{\text{B}}\text{u}^t$	705	2.6 (6H)	-25 to -80	$1.1 \times 10^{-4}$ ( $9.5 \times 10^{-5}$ )	61 (59)	13.7 (13.6)
Et	Et	$\text{Et}_2\dot{\text{P}}$	705	2.1 (4H)	-40 to -96	$1.0 \times 10^{-2}$ ( $8.3 \times 10^{-3}$ )	45 (44)	11.5 (11.2)
Pr <sup>n</sup>	Pr <sup>n</sup>	$\text{Pr}^n_2\dot{\text{P}}$	703	2.1 (4H)	-33 to -101	$4.0 \times 10^{-3}$ ( $6.5 \times 10^{-3}$ )	49 (44)	12.5 (10.9)
n-Octyl	n-Octyl	(n-Octyl) <sub>2</sub> $\dot{\text{P}}$	703 <sup>d</sup>	Unresolved	-31 to -95	$1.0 \times 10^{-2}$	45	11.4
Pr <sup>i</sup>	Pr <sup>i</sup>	$\text{Pr}^i_2\dot{\text{P}}$	703	1.9 (2H)	-44 to -111	$4.3 \times 10^{-2}$ ( $6.0 \times 10^{-2}$ )	44 (46)	12.0 (12.5)
Bu <sup>t</sup>	Bu <sup>t</sup>	$\text{Bu}^t_2\dot{\text{P}}$	714 <sup>d</sup>		-25 to -90	$1.5 \times 10^{-3}$ ( $1.4 \times 10^{-3}$ )	54 (50)	12.4 (12.3)
Allyl	Allyl	$\text{Allyl}_2\dot{\text{P}}$	708	1.8 (4H)	-102 to -123	$2.7 \times 10^2$	31	11.3
Me	Bu <sup>t</sup>	$\text{MeBu}^t\text{POBu}^t$	715	2.9 (3H)	-73 to -123	$4.1 \times 10^{-1}$	38	11.3
Et	Bu <sup>t</sup>	$\text{EtBu}^t\text{POBu}^t$	711	2.3 (2H)	-65 to -125	2.0	36	10.9
Pr <sup>i</sup>	Bu <sup>t</sup>	$\text{Pr}^i\text{Bu}^t\text{POBu}^t$	708	1.9 (1H)	-103 to -119	$4.8 \times 10^{-1}$	35	10.1
Me	Pr <sup>i</sup>	$\text{MePPr}^i_2$	715	3.0 (3H)	-51 to -102	$1.6 \times 10^{-2}$	46	12.2

<sup>a</sup> Determined at -70° unless otherwise stated and calculated using the Breit-Rabi equation. <sup>b</sup> The values of  $k_{\text{obs}}$  and  $A^{\text{obs}}$  given are half the measured values since the alkyl radical produced by  $\alpha$ -scission will be rapidly scavenged by a second phosphoranyl radical.<sup>2</sup> The values of  $E_a$  and  $\log_{10} A$  are considered accurate to  $\pm 2$  kJ mol<sup>-1</sup> and  $\pm 0.5$ , respectively. <sup>c</sup> Results in parentheses were determined in ref. 2 over smaller temperature ranges without the aid of computer averaging techniques. <sup>d</sup> At -100°.

approaching their equilibrium concentrations.<sup>2</sup> With this assumption, and providing  $K_1$  and  $K_2$  are very small, equation (3) may be obtained, in which  $K_1 = (k_1/k_{-1})$  and  $K_2 = (k_2/k_{-2})$ . Alkyl groups are less apicophilic<sup>3</sup> than

$$k_{\text{obs}} = K_1 k_4 + K_2 k_5 \quad (3)$$

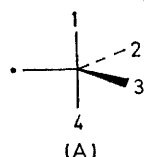
alkoxy-ligands, and thus it seems likely that the exchanges described by  $k_{-1}$  and  $k_{-2}$  will be faster than the exchange of identical ligands, which has been shown to take place very rapidly in a number of phosphoranyl radicals.<sup>3,7-9</sup>

If  $R^1 = R^2$  in (II), equation (3) simplifies to (4). The different decay rates of (II) may now be rationalised in the following manner. If, in the absence of appreciable

$$k_{\text{obs}} = 2K_1 k_4 \quad (4)$$

steric effects,  $K_1$  and  $K_2$  do not vary substantially with the nature of the alkyl substituents, then changes in  $k_{\text{obs}}$  reflect changes in  $k_4$  and  $k_5$ . Thus, for the series of symmetrical radicals  $R_2\dot{\text{P}}(\text{OBu}^t)_2$ ,  $k_{\text{obs}}$  increases  $R = \text{Me} < \text{Et}$ ,  $\text{Pr}^n$ , n-octyl  $< \text{Pr}^i < \text{allyl}$ , in line with the expected increase in  $k_4$  [equation (4)] as the stability of

\* The ligand sites are labelled as in (A).



and t-butyl radicals. The unfavourable steric interaction present in (III;  $R^1 = R^2 = \text{Bu}^t$ ) would be absent in (IIIa;  $R^1 = \text{Bu}^t$ ,  $R^2 = \text{Me}$ ) and  $K_1$  would have a similar value to that found for  $R_2\dot{\text{P}}(\text{OBu}^t)_2$  where steric effects are unimportant. However,  $k_4$ , the rate constant for cleavage of the apical P-Bu<sup>t</sup> bond in (IIIa;  $R^1 = \text{Bu}^t$ ,  $R^2 = \text{Me}$ ) would be large, and  $k_{\text{obs}}$  ( $\approx K_1 k_4$ ) would be expected to be larger than ( $k_{\text{obs}}/2$ ) for (II;  $R^1 = R^2 = \text{Pr}^i$ ), as observed by experiment. In contrast, (II;  $R^1 = \text{Pr}^i$ ,  $R^2 = \text{Me}$ ) decays to give isopropyl radicals less rapidly than (II;  $R^1 = R^2 = \text{Pr}^i$ ). Here  $K_1$  and  $k_4$  should be similar for both systems; if they were identical for both phosphoranyl radicals then  $k_{\text{obs}}$  for (II;  $R^1 = R^2 = \text{Pr}^i$ ) would be about twice the value for (II;  $R^1 = \text{Pr}^i$ ,  $R^2 = \text{Me}$ ). This latter result excludes the possibility that ligand sub-set symmetry effects,<sup>10,†</sup> which may be important in governing the

† Semi-empirical MO calculations suggest that an overall stabilisation of a trigonal bipyramidal phosphorane occurs when all the equatorial or both the apical ligands are identical.<sup>10</sup>

<sup>7</sup> P. J. Krusic and P. Meakin, *Chem. Phys. Letters*, 1973, **18**, 347.

<sup>8</sup> R. W. Dennis and B. P. Roberts, *J. Organometallic Chem.*, 1973, **47**, C8.

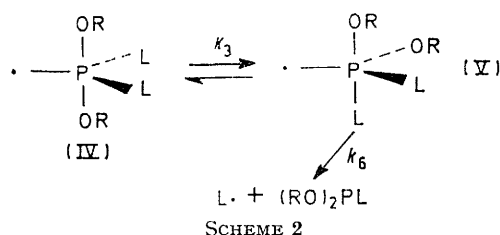
<sup>9</sup> I. H. Elson, M. J. Parrott, and B. P. Roberts, *J.C.S. Chem. Comm.*, 1975, 586.

<sup>10</sup> P. Gillespie, P. Hoffmann, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsois, and I. Ugi, *Angew. Chem. Internat. Edn.*, 1971, **10**, 687; F. Ramirez and I. Ugi, *Bull. Soc. chim. France*, 1974, 453.

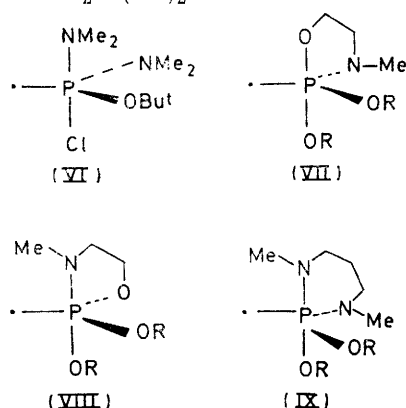
stability of the related phosphoranes ( $PX_5$ ), could be responsible for the rapid decay of (II;  $R^1 = Bu^t$ ,  $R^2 = Me$ ) compared with that of (II;  $R^1 = R^2 = Bu^t$ ).

(c)  $\alpha$ -Scission of Radicals  $R_2\dot{P}(OEt)OBu^t$  and  $R_2\dot{P}(OEt)_2$ .—The phosphoranyl radicals  $R_2\dot{P}(OBu^t)_n(OEt)_{2-n}$  and  $(Me_2N)_2\dot{P}(OBu^t)_n(OEt)_{2-n}$  ( $n = 0-2$ ) exhibit decreased stability towards  $\alpha$ -scission, with loss of  $R\cdot$  and  $Me_2N\cdot$  radicals respectively, as the number of ethoxy-ligands increases.<sup>2,3</sup> This trend extends to the related arsoranyl radicals,<sup>11</sup> where  $Ph_2\dot{As}(OEt)OBu^t$  decays to give phenyl radicals 40 times more rapidly at  $-100^\circ$  than  $Ph_2\dot{As}(OBu^t)_2$ .\*

These results may be explained on the basis of isomerisation of the detected phosphoranyl or arsoranyl radical occurring prior to fragmentation.



We suggest that the increase in  $k_{obs} [= (k_6 K_3)/(1 + K_3)]$ , for a given L, which occurs as the proportion of ethoxy-substituents increases, is mainly the result of an increase in  $K_3$ , the associated change in  $k_6$  being smaller, although not negligible (see below). As one ligand is changed from t-butoxy to ethoxy (which is less bulky and probably a poorer electron donor than the former ligand) it appears to become more favourable for a ligand of relatively low electronegativity to occupy an apical site.<sup>3</sup> For example,<sup>3</sup>  $K_3$  is much larger for  $(EtO)_2\dot{P}(NMe_2)_2$  than for  $(Bu^tO)_2\dot{P}(NMe_2)_2$ . The radical  $Bu^tO(Cl)\dot{P}(NMe_2)_2$ , which has a relatively electronegative chlorine substituent, appears to exist only as the isomer (VI) according to e.s.r. spectroscopy.<sup>12</sup> These trends probably extend to  $R_2\dot{P}(OR)_2$  and  $Ph_2\dot{As}(OR)_2$ .



The relative importance of steric and electronic effects in determining such configurational preferences is difficult to assess. However, we have previously shown<sup>3</sup> that

\* At  $-100^\circ$   $Ph_2\dot{As}(OMe)OBu^t$  decayed 700 times more rapidly than  $Ph_2\dot{As}(OBu^t)_2$ .<sup>11</sup>

the isomer ratio  $[(VIII)] : [(VII)]$  depends markedly upon whether the acyclic alkoxy substituents are ethoxy- or t-butoxy-groups { $R = Et$ ,  $[(VIII)] : [(VII)] = 0.33$ ;  $R = Bu^t$ ,  $[(VIII)] : [(VII)] = 0.026$  at  $-95^\circ$ }.

If steric effects were predominant, it seems likely that (VIII) would be favoured relative to (VII) by more bulky substituents and hence we believe that an electronic effect is mainly responsible for the increase in the ratio  $[(VIII)] : [(VII)]$  on going from  $R = Bu^t$  to  $R = Et$ , although further work is required.

We have measured the rate constants for  $\alpha$ -scission of two cyclic aminophosphoranyl radicals (IX;  $R = Et$  or  $Bu^t$ ), in which the six-membered ring bridges apical and equatorial sites in the most stable isomers.<sup>3</sup> The results, together with those for related systems are given in Table 2.

TABLE 2

First-order decay rate constants for some dialkoxybis-(dialkylamino)phosphoranyl radicals in cyclopropane

Phosphoranyl radical	$k_{obs}^{a,b}/s^{-1}$ at $-100^\circ$	$E_a^{obs}/kJ\ mol^{-1}$	$\log_{10}(A^{obs}/s^{-1})$
$(EtO)_2\dot{P}(NMe_2)_2$ <sup>c</sup>	$1.5 \times 10^2$ (20 <sup>d</sup> )		
$EtO(Bu^tO)\dot{P}(NMe_2)_2$ <sup>c</sup>	$2.5 \times 10^2$ (6.5 <sup>d</sup> )	$31 \pm 4$	$11.7 \pm 1.0$
$(Bu^tO)_2\dot{P}(NMe_2)_2$	$3.4$ (0.12 <sup>d</sup> )	$45.3 \pm 2$ (38)	$14.2 \pm 0.5$ (12.5)
(IX; $R = Et$ )	$4 \times 10^2$	$22 \pm 8$	$9.4 \pm 2.0$
(IX; $R = Bu^t$ )	$6 \times 10^2$	$26 \pm 8$	$10.9 \pm 2.0$

<sup>a</sup> If the major process removing the dialkylaminyl radicals produced by  $\alpha$ -scission is reaction with the phosphoranyl radicals, then the given rate constant could be up to twice that for  $\alpha$ -scission. <sup>b</sup> Values in parentheses are taken from ref. 3. <sup>c</sup> Two isomers of the phosphoranyl radical were present and both decayed with the same rate constant, within experimental accuracy. <sup>d</sup> At  $-125^\circ$ .

For the radical  $(Bu^tO)_2\dot{P}(NMe_2)_2$   $K_3$  is very small [(V) is undetectable by e.s.r. spectroscopy], whilst for  $(EtO)_2\dot{P}(NMe_2)_2$  the species (V) is the predominant isomer<sup>3</sup> at  $-125^\circ$ . In agreement with the proposal that  $Me_2N\cdot$  radicals are produced mainly by homolysis of the apical P-N bond in (V;  $L = Me_2N$ ), the phosphoranyl radical  $(Bu^tO)_2\dot{P}(NMe_2)_2$  decays much more slowly than  $(EtO)_2\dot{P}(NMe_2)_2$ . However, when a P-N bond is constrained to be apical in (IX),  $k_{obs}$  is large for both (IX;  $R = Et$ ) and (IX;  $R = Bu^t$ ), with the latter now somewhat less stable towards  $\alpha$ -scission. Thus when the change of alkoxy-groups does not affect the position of the configurational equilibrium it is apparent that t-butoxy- and ethoxy-substituted phosphoranyl radicals undergo  $\alpha$ -scission at similar rates, with the former species now undergoing fragmentation somewhat more readily. Both electronic and steric effects are probably responsible for the lower stability of the t-butoxy-analogues.

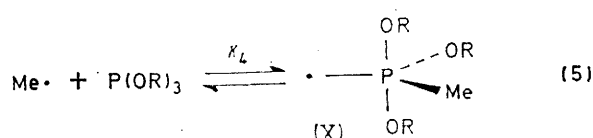
(d) *Electronic and Steric Effects on the Rate of  $\alpha$ -Scission. Stereochemical Non-rigidity of Phosphoranyl Radicals.*—Since  $\alpha$ -scission of a phosphoranyl radical involves a reduction in the number of ligands around phosphorus

<sup>11</sup> E. Furimsky, J. A. Howard, and J. R. Morton, *J. Amer. Chem. Soc.*, 1973, **95**, 6574.

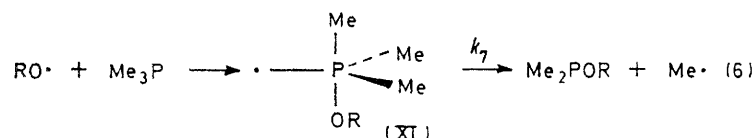
<sup>12</sup> I. G. Neil, unpublished results.

we might expect to find evidence of steric acceleration for this mode of fragmentation.

Methyl radicals, generated photochemically from azomethane, add reversibly to trialkyl phosphites<sup>13</sup> to produce the phosphoranyl radicals  $\text{MeP}(\text{OR})_3$  (X).



The radical concentration ratio  $[(\text{X})]:[\text{Me}\cdot]$  was measured as a function of incident light intensity, and was



found to be effectively constant at light intensities for which both radicals were readily detectable by e.s.r. spectroscopy. It may be shown that as the light intensity, and thus the radical concentration, tends to zero the expression  $[(\text{X})]:[\text{Me}\cdot][\text{P}(\text{OR})_3]$  tends to the equilibrium constant  $K_4$ , the values of which are gathered in Table 3.

TABLE 3

Equilibrium constants for the association of methyl radicals with trialkyl phosphites in cyclopentane at  $-70^\circ$

Phosphoranyl radical (X)	$K_4/\text{l mol}^{-1}$
$\text{MeP}(\text{OEt})_3$	120
$\text{MeP}(\text{OPr}^i)_3$	19
$\text{MeP}(\text{OBu}^t)_3$	$<0.1^a$
$\text{MeP}(\text{OCH}_2\text{Bu}^t)_3$	115

<sup>a</sup> Whilst a strong spectrum of the methyl radical was observed, no signal from the phosphoranyl radical could be detected for a phosphite concentration of 0.5M. The weak signal from a phosphorus-centred radical reported in ref. 13 was not obtained in the present work.

The degree of dissociation of (X) increases along the series  $\text{R} = \text{Et} < \text{Pr}^i < \text{Bu}^t$ , as noted qualitatively previously,<sup>13</sup> but the relative importance of steric and electronic effects is again difficult to assess. There is only a relatively small decrease in the value of  $K_4$  (from 120 to 115  $\text{l mol}^{-1}$ ) on going from triethyl phosphite to trineopentyl phosphite, which both contain primary alkoxy-groups. However, the increase in bulk on going from ethoxy to neopentoxy is relatively far removed from phosphorus.

From the temperature variation of the equilibrium constant for the association of methyl radicals with triisopropyl phosphite we find  $\Delta H_5^\circ -29 \text{ kJ mol}^{-1}$  and  $\Delta S_5^\circ -119 \text{ J K}^{-1} \text{ mol}^{-1}$  in the temperature range  $-40$  to  $-90^\circ$  in cyclopentane solution, providing, we believe, the first measurement of a bond dissociation enthalpy for a phosphoranyl radical.

The influence of electronic effects on the rate of  $\alpha$ -

\* Photolysis of azomethane in the presence of  $\text{Me}_2\text{POBu}^t$  gave rise to the e.s.r. spectrum of (XI;  $\text{R} = \text{Bu}^t$ ) showing that  $\alpha$ -scission of this phosphoranyl radical is reversible.<sup>14</sup>

scission of phosphoranyl radicals is perhaps most clearly demonstrated by comparison of the rates of fragmentation of (V;  $\text{R} = \text{Et}$ ,  $\text{L} = \text{Me}_2\text{N}$ ) and (IX;  $\text{R} = \text{Et}$  or  $\text{Bu}^t$ ) with that of (VI). The chlorine-containing radical (VI) is much more stable<sup>12</sup> towards loss of  $\text{R}_2\text{N}\cdot$  than the alkoxyaminophosphoranyl radicals, and the e.s.r. spectrum of (VI) may be readily detected even at  $-20^\circ$ . The relatively electronegative chlorine substituent thus retards cleavage of the *trans*-apical P-N bond.

We have also examined the rates of  $\alpha$ -scission of three alkoxy radical adducts of trimethylphosphine, (XI;  $\text{R} = \text{Et}$ ,  $\text{Bu}^t$ , or *t*-pentyl).

An apical methyl group is always present in (XI) and

thus no isomerisation is necessary prior to fragmentation. The rate constants for decay of (XI) are given in Table 4.

TABLE 4

E.s.r. parameters and first-order decay rate constants for the radicals  $\text{Me}_3\text{POR}$  (XI)

R in (XI)	Solvent <sup>a</sup>	Hyperfine splittings/G at $-110^\circ$		$k_7^b/\text{s}^{-1}$ at $-100^\circ$
		$a(\text{P})$	$a(\text{H})$	
$\text{MeCH}_2$ -	C	595 <sup>c</sup>	4.6 (3H) 3.2 (6H)	21.0
$\text{Me}_3\text{C}$ -	C	611 <sup>c</sup>	4.63 (3H) 2.67 (6H)	32.3 <sup>d</sup>
$\text{Me}_3\text{C}$ -	T			1.6
$\text{EtMe}_2\text{C}$ -	C	610	4.6 (3H) 2.7 (6H)	40.2

<sup>a</sup> C = Cyclopropane, T = toluene. <sup>b</sup> If the major process removing the methyl radicals produced by  $\alpha$ -scission is their reaction with (XI), the observed rate constant given could be up to  $2k_7$ . <sup>c</sup> At  $-80^\circ$ . <sup>d</sup> The temperature dependence of  $k_7$  over the range  $-50$  to  $-100^\circ$  was described by  $\log_{10}(k_7/\text{s}^{-1}) = 8.2 - 24/\theta$ , but the Arrhenius plot showed some curvature, probably due to the effects of cage return (see text), and the activation parameters are unreliable.

The rates of decay of (XI;  $\text{R} = \text{Et}$ ,  $\text{Bu}^t$ , or *t*-pentyl) are rather similar, in marked contrast to those for the detected isomers of  $\text{R}_2\text{P}(\text{OR})_2$  where  $\text{R} = \text{Et}$  or  $\text{Bu}^t$  (see above). The small differences in rates of  $\alpha$ -scission for (XI) may be ascribed to steric and/or electronic effects. However, the radical (XI;  $\text{R} = \text{Bu}^t$ ) decayed more slowly in toluene than in the less viscous cyclopropane, suggesting that cage return is probably important,\* at least in toluene solution, and hence conclusions based upon small differences in rate in cyclopropane will not be meaningful.

In summary, electronic effects are important for the  $\alpha$ -scission of phosphoranyl radicals, as expected, but the small rate differences between ethoxy- and *t*-butoxy-substituted species, when configurational effects are absent, are difficult to assign to steric or electronic effects.

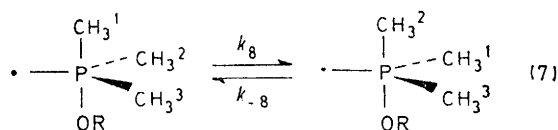
Temperature-dependent line-shape effects were detectable in the e.s.r. spectra of (XI;  $\text{R} = \text{Et}$ ,  $\text{Bu}^t$ , or *t*-pentyl)

<sup>13</sup> A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 2224.

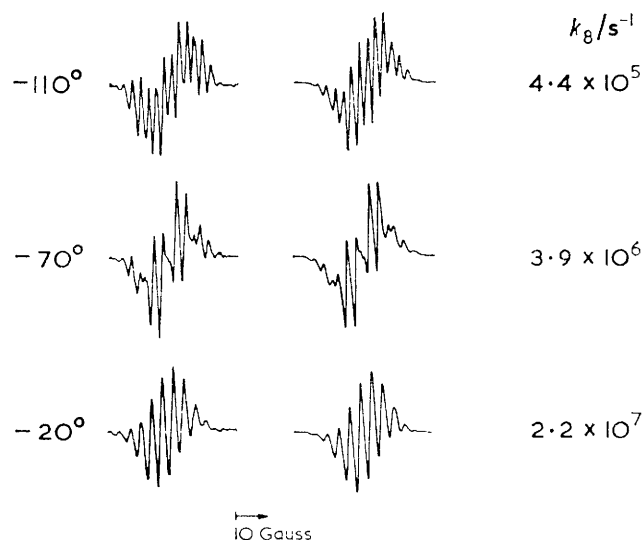
<sup>14</sup> R. W. Dennis, unpublished results.



and are consistent with increasingly rapid exchange of apical and equatorial methyl groups as the temperature was increased [see equation (7)], such that the alkyl groups are equivalent on the e.s.r. time scale above about  $-30^\circ$  for all three radicals. Typical spectra for (XI);



R = Bu<sup>t</sup>) and their computer simulations are shown in the Figure.



E.s.r. spectra (left) and their computer-simulations (right) for the radical  $\text{Me}_3\text{POBu}^t$  in cyclopropane. Only the low field [ $m_1(^{31}\text{P}) = +\frac{3}{2}$ ] lines are shown and the simulations were obtained using the coupling constants given in Table 4 with a natural line-width of 1.5 G

The temperature-dependence of  $k_8$  (R = Bu<sup>t</sup>) may be expressed by equation (8) where  $\theta = 2.303RT$  kJ mol<sup>-1</sup>, and at  $-70^\circ$   $k_8 = 4 \times 10^6$  s<sup>-1</sup>.

$$\log_{10} (k_8/\text{s}^{-1}) = (10.4 \pm 1) - (15 \pm 4)/\theta \quad (8)$$

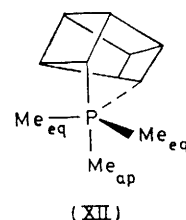
The rate of methyl ligand exchange appeared to be almost independent of the nature of the alkoxy-groups. The phosphorane (XII) undergoes methyl ligand exchange at a similar rate ( $k_{\text{exch}}$  ca.  $10^2$  s<sup>-1</sup> at  $-167^\circ$ ) as judged from the temperature dependence of its n.m.r. spectrum<sup>15</sup> (for  $\text{Me}_3\text{POBu}^t$  the value of  $k_8$  extrapolated to  $-167^\circ$  is  $10^3$  s<sup>-1</sup>). This similarity of rates<sup>3,7-9,16</sup> does not, of course, necessarily imply similarity of mechanisms for ligand exchange in  $\cdot\text{PX}_4$  and  $\text{PX}_5$ .

(e)  $\alpha$ -Scission of Trialkyl-*t*-butoxyphosphoranyl Radicals. —The primary phosphoranyl radicals  $\text{Bu}^t\text{OPR}_3$ , produced by photolysis of di-*t*-butyl peroxide in the presence of trialkylphosphines, are very unstable towards  $\alpha$ -scission if R is a higher alkyl group than methyl,<sup>2</sup> and

<sup>15</sup> C. H. Bushweller, H. S. Bilofsky, E. W. Turnblom, and T. J. Katz, *Tetrahedron Letters*, 1972, 2401.

<sup>16</sup> R. Luckenbach, 'Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements,' G. Thieme, Stuttgart, 1973.

these radicals are generally very difficult to detect by e.s.r. spectroscopy. The secondary species,  $(\text{Bu}^t\text{O})_2\text{PR}_2$ ,

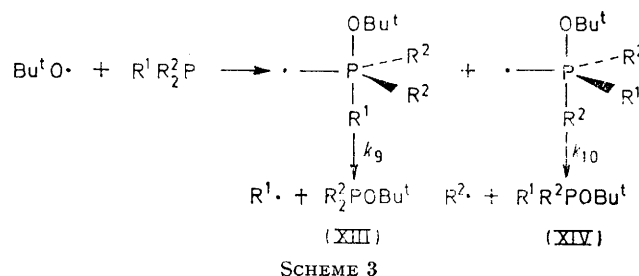


produced by addition of *t*-butoxyl radicals to the  $\text{Bu}^t\text{OPR}_2$  generated by  $\alpha$ -scission of the primary phosphoranyl radical, is readily detectable.<sup>2</sup>

We have estimated the relative rates of generation of the different alkyl radicals produced by  $\alpha$ -scission of the primary phosphoranyl radical adducts between *t*-butoxyl radicals and a series of trialkylphosphines with mixed alkyl groups (see Scheme 3 which assumes that phosphoranyl radical fragmentation occurs primarily by cleavage of an apical P-C bond).

The relative concentrations of alkyl radicals during steady irradiation, determined at low conversion to eliminate interference from secondary reactions, were essentially independent of temperature over the range  $-30$  to  $-90^\circ$ , and these results are given in Table 5.

If the self- and cross-reactions of these simple alkyl radicals are assumed to occur with similar rate constants at close to the diffusion-controlled limit,<sup>17</sup> it follows that



the steady-state concentration ratio ( $[\text{R}^1\cdot] : [\text{R}^2\cdot]$ ) is equal to the ratio of the rates of formation of  $\text{R}^1\cdot$  and  $\text{R}^2\cdot$ .

TABLE 5

Alkyl radical concentration ratios obtained during continuous u.v. irradiation of mixtures of trialkylphosphines and di-*t*-butyl peroxide in cyclopropane at  $-50^\circ$

Phosphine	$[\text{R}^1\cdot] : [\text{R}^2\cdot]^a$
$\text{Bu}^t\text{Me}_2\text{P}$	$[\text{Bu}^t\cdot] : [\text{Me}\cdot] > 10$
$\text{Bu}^t\text{Et}_2\text{P}$	$[\text{Bu}^t\cdot] : [\text{Et}\cdot] \quad 2.0 \pm 0.1$
$\text{Bu}^t\text{Pr}^n\text{P}$	$[\text{Bu}^t\cdot] : [\text{Pr}^n\cdot] \quad 1.2 \pm 0.1$
$\text{Bu}^t\text{Bu}^n\text{P}$	$[\text{Bu}^t\cdot] : [\text{Bu}^n\cdot] \quad 1.1 \pm 0.1$
$\text{Bu}^t\text{Pr}^i\text{P}$	$[\text{Bu}^t\cdot] : [\text{Pr}^i\cdot] \quad 0.8 \pm 0.1$
$\text{Bu}^t\text{EtP}$	$[\text{Bu}^t\cdot] : [\text{Et}\cdot] \quad 4.0 \pm 0.2$
$\text{Bu}_2^t\text{Bu}^n\text{P}$	$[\text{Bu}^t\cdot] : [\text{Bu}^n\cdot] \quad 2.0 \pm 0.1$
$\text{Bu}_2^t\text{EtP}$	$[\text{Bu}^t\cdot] : [\text{Et}\cdot] \quad 3.0 \pm 0.2$

<sup>a</sup> Ratios independent of temperature within experimental error between  $-30$  and  $-90^\circ$ .

Apart from the reaction of *t*-butoxyl radicals with dimethyl-*t*-butylphosphine which gives only *t*-butyl radicals in detectable concentration, the overall  $\text{S}_{\text{H}2}$

<sup>17</sup> D. Griller and K. U. Ingold, *Internat. J. Chem. Kinetics*, 1974, **6**, 453.

reaction of *t*-butoxyl radicals with  $R^1R_2^2P$  is unselective. The question arises as to whether or not the two isomers of  $R^1R_2^2POBu^t$  have time to interconvert prior to undergoing  $\alpha$ -scission, because if they do not the product alkyl radical ratio is determined in the phosphoranyl formation step and will not reflect the relative magnitudes of  $k_9$  and  $k_{10}$ .

The e.s.r. spectrum of  $Et_3POBu^t$  is only just detectable <sup>2</sup> at  $-145^\circ$ , at which temperature the rate constant for its  $\alpha$ -scission must be *ca.*  $10^3 \text{ s}^{-1}$ . Assuming a frequency factor of  $10^{12}$ – $10^{13} \text{ s}^{-1}$  this rate constant would be *ca.*  $10^6 \text{ s}^{-1}$  at  $-70^\circ$ , although this estimate is clearly subject to a large error. Most of the phosphoranyl radicals listed in Table 5 are probably less stable towards  $\alpha$ -cleavage than  $Et_3POBu^t$ . The rate constant for exchange of apical and equatorial methyl groups in  $Me_3POBu^t$  is *ca.*  $4 \times 10^6 \text{ s}^{-1}$  at  $-70^\circ$  (see above). The low selectivity in the overall reaction may thus result mainly from the unselective formation of the intermediate phosphoranyl radicals,\* although the available kinetic data do not allow definite conclusions to be drawn at present. If the apical alkyl group is methyl the phosphoranyl radical might live long enough for alkyl group exchange to occur before  $\alpha$ -cleavage.

On the basis of our results with the phosphoranyl radicals  $(Bu^tO)_2PR_2$ , we might have expected the ratio  $[Bu^t]:[Et]$  for the reaction of *t*-butoxyl radicals with  $Bu^t_2PEt$  to be appreciably less than twice that for the corresponding reaction with  $Bu^tPEt_2$ , on account of the unfavourable steric interaction between apical and equatorial *t*-butyl groups in (XIV;  $R^1 = Et$ ,  $R^2 = Bu^t$ ). The experimental result is consistent with the product alkyl radical ratio being determined primarily in the unselective phosphoranyl formation step, although the importance of other factors such as loss of alkyl radicals from equatorial sites, which may be more important with  $R_3POBu^t$  than  $R_2P(OBu^t)_2$ , remains to be assessed.

## EXPERIMENTAL

The generation of transient free radicals by photolytic methods for e.s.r. study and the kinetic methods employed have been described previously.<sup>2,3</sup> The syntheses of new organophosphorus compounds are described below.

*Di-isopropyl-t-butylphosphine* was prepared by addition of isopropyl-lithium (12 g) in pentane (200 ml) to a solution of dichloro-*t*-butylphosphine (18 g) in benzene (250 ml) at room temperature with stirring. After the addition the mixture was refluxed for 17 h, cooled, and water (15 ml) was added. The organic phase was dried ( $MgSO_4$ ) and, after the solvent was removed, distillation yielded the phosphine (10 g, 60%), b.p.  $77$ – $79^\circ$  at 10 mmHg. The phosphine was analysed as the *methylphosphonium iodide*,  $[Bu^tPPr^i_2Me]^+I^-$ ,

\* The overall reaction  $Bu^tO \cdot + PR_3 \longrightarrow Bu^tOPR_2 + R \cdot$  has  $\Delta H^\circ$  *ca.*  $-92 \text{ kJ mol}^{-1}$  (ref. 1) and is extremely rapid in solution.<sup>2</sup> The P–C bond in  $CH_3P(OR)_3$  is extremely weak (see text) and it seems likely that  $\Delta H^\circ$  is close to zero for the reaction  $Bu^tOPR_3 \longrightarrow R \cdot + Bu^tOPR_2$ . Hence  $\Delta H^\circ$  will be *ca.*  $-90 \text{ kJ mol}^{-1}$  for the phosphoranyl formation step  $Bu^tO \cdot + PR_3 \longrightarrow Bu^tOPR_3$ , and this reaction will be irreversible occurring at close to the diffusion-controlled limiting rate in solution.<sup>2</sup> The high exothermicity and low activation energy for the formation step is consistent with its probable low configurational selectivity with respect to placement of the alkyl groups.

prepared by addition of methyl iodide in acetone (Found: C, 41.8; H, 8.2; P, 9.8; I, 40.4.  $C_{11}H_{26}PI$  requires C, 41.8; H, 8.3; P, 9.9; I, 40.1%). Other trialkylphosphines were analysed as similar derivatives.

*Ethyl-di-n-butylphosphine*, b.p.  $82$ – $83^\circ$  at 8 mmHg [Found (for methylphosphonium iodide): C, 41.8; H, 8.3; P, 10.2; I, 40.4.  $C_{11}H_{26}PI$  requires C, 41.8; H, 8.3; P, 9.8; I, 40.1%], was prepared from dichloroethylphosphine and butylmagnesium bromide in ether. *Di-t-butyl-n-butylphosphine*, b.p.  $88$ – $90^\circ$  at 8 mmHg [Found (for methylphosphonium iodide): C, 45.6; H, 8.9; P, 9.2; I, 37.2.  $C_{13}H_{30}PI$  requires C, 45.4; H, 8.8; P, 9.0; I, 36.9%], was prepared from chlorodi-*t*-butylphosphine and *n*-butyllithium in *n*-pentane.

*Chloro(isopropyl)-t-butylphosphine* was prepared by dropwise addition with stirring of isopropylmagnesium chloride [from isopropyl chloride (33 g) and magnesium (12 g) in ether (150 ml)] to dichloro-*t*-butylphosphine (25 g) in ether (500 ml) maintaining the temperature between  $-70$  and  $-80^\circ$ . After the addition the mixture was refluxed for 1 h, filtered, the ether removed and the residue distilled to yield the chlorophosphine, b.p.  $69$ – $71^\circ$  at 16 mmHg (Found: C, 50.2; H, 9.6; P, 18.3.  $C_7H_{16}PCl$  requires C, 50.4; H, 9.7; P, 18.6%).

Chloro(isopropyl)-*t*-butylphosphine (11.8 g) in ether (250 ml) was added dropwise to potassium *t*-butoxide (12 g) in ether (600 ml) and the mixture refluxed for 3 h. After filtration and removal of the solvent, distillation yielded *isopropyl-t-butoxy-t-butylphosphine* (10 g), b.p.  $32^\circ$  at 0.2 mmHg. Proton-decoupled  $^{31}P$  n.m.r. in  $C_6D_6$  showed a single resonance at  $\delta$   $-125.6$  p.p.m. relative to external 85%  $H_3PO_4$  (Found: C, 63.9; H, 12.0; P, 15.0.  $C_{11}H_{25}OP$  requires C, 64.7; H, 12.3; P, 15.2%).

The following compounds were prepared by similar reactions: *chloro(ethyl)-t-butylphosphine* b.p.  $42$ – $44^\circ$  at 9 mmHg (Found: C, 47.4; H, 9.4; P, 20.2.  $C_6H_{14}PCl$  requires C, 47.2; H, 9.2; P, 20.3%); *chloro(methyl)-t-butylphosphine*,<sup>18</sup> b.p.  $137$ – $139^\circ$  at 760 mmHg; *ethyl-t-butoxy-t-butylphosphine*, b.p.  $40^\circ$  at 2.4 mmHg (Found: C, 63.1; H, 12.1; P, 16.1.  $C_{10}H_{23}OP$  requires C, 63.1; H, 12.2; P, 16.3%). *Methyl-t-butoxy-t-butylphosphine*, b.p.  $57$ – $59^\circ$  at 19 mmHg, prepared in a similar manner, was unstable and could not be obtained analytically pure (Found: C, 58.3; H, 11.5; P, 18.0.  $C_9H_{21}OP$  requires C, 61.3; H, 12.0; P, 17.6%). The decomposition products were methyl-*t*-butylphosphine oxide and isobutene. The  $^{31}P$  n.m.r. spectrum in  $C_6D_6$  of the freshly-distilled material showed a major resonance at  $\delta$   $-106$  p.p.m., with a smaller signal at  $\delta$   $-40$  p.p.m. ( $^1J_{P-H}$  438 Hz) assigned to the phosphine oxide. A sample gave a good analysis for the phosphine oxide (Found: C, 50.1; H, 10.9.  $C_5H_{13}OP$  requires C, 50.0; H, 10.9%) after storage at room temperature for one week.

The computer-simulations of the spectra of  $Me_3POR$  showing the effects of methyl ligand exchange were obtained using the program ESREXN written by Dr. J. Heinzer and obtained from QCPE at the University of Indiana.

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[5/1693 Received, 2nd September, 1975]

<sup>18</sup> O. J. Scherer and W. Gick, *Chem. Ber.*, 1970, **103**, 71.