Free Radical Studies of Organophosphorus Compounds. VI. Formation, Permutation, and β Scission of Tetraalkoxyphosphoranyl Radicals, $(RO)_4P\cdot$[1]

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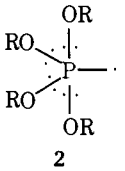
Abstract: A series of phosphoranyl radicals $R^1O(R^2O)\dot{P}(OEt)_2$ has been generated both by reaction of $R^1O\cdot$ with $R^2O\text{-}P(OEt)_2$ and reaction of $R^2O\cdot$ with $R^1OP(OEt)_2$. The ratio of phosphates, $R^1OP(O)(OEt)_2$ and $R^2OP(O)(OEt)_2$, formed on β scission of a given intermediate phosphoranyl radical depends on the pathway of generation of $R^1O(R^2O)\dot{P}(OEt)_2$. This "memory" effect is taken to rule out: (1) tetrahedral geometry for the phosphoranyl radical; (2) random introduction of attacking RO· into apical and equatorial positions of trigonal-pyramidal intermediate **2**; (3) accidentally equal β-scission rates at both positions; (4) permutation of alkoxy groups between apical and equatorial positions at a rate faster than β scission. It is estimated that $\Delta G^{\ddagger}$ for apical–equatorial alkoxy exchange, if it occurs at all in noncyclic tetraalkoxyphosphoranyl radicals of the type studied, must be greater than 10–12 kcal/mol. This is considered to be a higher barrier than that expected for $(RO)_5P$ systems and suggests that phosphoranyl radicals cannot be considered as simply analogous to their pentacovalent phosphorus counterparts. A mechanism in which apical–equatorial alkoxy permutation must precede β scission is ruled out by the results. A model is proposed in which nonfluxional phosphoranyl radicals undergo β scissions at both apical and equatorial positions but more rapidly apical. A consistent set of relative β-scission rate constants for ethoxy, *sec*-BuO, and *sec*-PentO substituents is derived which allows calculation of the experimental phosphate ratios for eight reactions with an average error of 6%.

Several groups of workers have established by ESR spectroscopy that tetraalkoxyphosphoranyl radicals[2] (**1**) are formed when alkoxy radicals are generated in the presence of trialkyl phosphites (eq 1).[3] These species are presumably

$$R'O\cdot + (RO)_3P \xrightarrow{a} \underset{\mathbf{1}}{R'O\dot{P}(OR)_3} \xrightarrow{b} R'\cdot + (RO)_3PO \quad (1)$$

intermediates in reaction 1 which, as depicted, gives product trialkyl phosphate via a C–O bond scission process termed β scission. The kinetics of phosphoranyl radical decay have been studied thoroughly by ESR techniques.[3b,c,e-g,i,4]

The configuration normally ascribed[3] to the tetraalkoxyphosphoranyl radical is that of a trigonal bipyramid (TBP). Most usually an electronic structure with the odd electron in an orbital with electron density primarily in the equatorial plane has been written, **2**. An important alternative limiting structure, **3**, is one based on hypervalent bonding princi-



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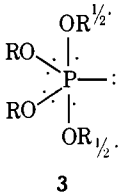

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ples in which the odd electron resides in a largely nonbonding molecular orbital distributed over the apical ligands. Requisite 3s spin density on phosphorus can be obtained, in this view, by mixing into the highest energy MO a contribution from the phosphorus 3s atomic orbital.[5] It is likely that the true bonding picture depends greatly on the nature of the substituents on phosphorus. In any case, the geometry remains near-trigonal-bipyramidal, and we will arbitrarily utilize structures like **2** in this paper. The ESR results are the basis of the assumption we make in our studies that the odd electron (or pair) is preferentially equatorial in **1**.

If the odd electron (or pair) is viewed as a phantom ligand, then the structural similarity of phosphoranyl radicals **2** and **3** to truly pentacovalent phosphoranes is obvious. Despite this similarity, there is no reason to conclude a priori that phosphoranyl radicals and phosphoranes need be alike in all their structural properties. The phosphoranes have been studied extensively, and among their more notable properties is the ease with which the positions of the substituents on phosphorus are permuted intramolecularly.[6] It is also often found useful to assume that in forming phosphoranes, the final ligand enters the trigonal bipyramid apically. These questions of the introduction and possible positional permutations of substituents between apical and equatorial sites in phosphoranyl radicals have received only a little attention.[1c,3e]

If the odd electron is kept in the equatorial position, as ESR suggests, then the notation of Musher[7] allows us to distinguish the possible stereochemical modes for permuta-

Scheme I

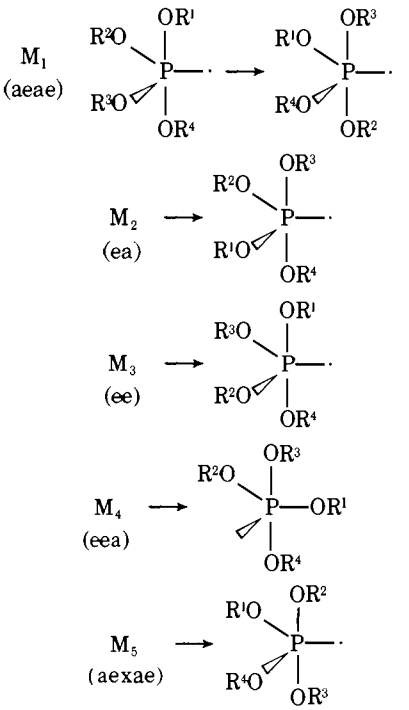


Table I. Phosphate Product Ratios from Reaction 2

Case	Reactants				Products[f]		
	$R^1O\cdot$	$R^2O\cdot$	$R^2OP(OEt)_2$	$R^1OP(OEt)_2$	$R^2OP(O)(OEt)_2/R^1OP(O)(OEt)_2$	$R^2OP(O)(OEt)_2/R^1O(R^2O)P(O)OEt$	% yield[k]
1[a]	$C_6H_5CH_2O\cdot$		*p*-$MeC_6H_4CH_2OP(OEt)_2$		1.15 ± 0.02 (15)		87–99
2[a]		*p*-$MeC_6H_4CH_2O\cdot$		$C_6H_5CH_2OP(OEt)_2$	0.80 ± 0.02 (10)		92–99
3[b,c]	*sec*-BuO·		$(EtO)_3P$		1.07 ± 0.04 (8)		83–91
4[b,d]		EtO·		*sec*-$BuOP(OEt)_2$	0.75 ± 0.02 (8)		88–93
5[b,e]	*sec*-BuO·		$(EtO)_3P$		0.96 ± 0.01 (10)		80–90
6[b,e]		EtO·		*sec*-$BuOP(OEt)_2$	0.79 ± 0.01 (7)		89–92
7[a]	*sec*-PentO·		$(EtO)_3P$		1.27 ± 0.01 (2)		96, 96
8[a]		EtO·		*sec*-PentOP-$(OEt)_2$	0.95 ± 0.01 (2)		95, 97
9[a]	*sec*-BuO·		*sec*-$PentOP(OEt)_2$		1.03 ± 0.03 (4)	1.62 ± 0.03 (4)	93–95
10[a]		*sec*-PentO·		*sec*-$BuOP(OEt)_2$	0.74 ± 0.05 (4)	1.26 ± 0.10 (4)	89–94
11[a]	EtO·		(*sec*-PentO)(*sec*-BuO)POEt		0.83 ± 0.02 (10)[g]	1.32 ± 0.04 (10)[h]	87–94
12[a]	*sec*-BuO·		(*sec*-BuO)(*sec*-PentO)POEt		1.88 ± 0.10 (4)[i]	7.15 ± 0.58 (4)[j]	92–98

[a] Solutions mostly 0.23 to 1.2 M in phosphite and 0.4 to 0.6 M in initial hyponitrite, $R^1ON_2OR^1$ or $R^2ON_2OR^2$ in benzene, degassed and heated at 65 °C. [b] In both benzene and alkane solvents; see Table III. [c] Includes two experiments where hyponitrite was photolyzed at 16 °C; see Table III. [d] Includes three experiments in which hyponitrite was photolyzed at 16 °C; see Table III. [e] Alkoxy radicals generated photolytically at 16 °C from the peroxide, ROOR. [f] Replicate ratios; number of replications in parentheses; average errors given. [g] *sec*-$PentOP(O)(OEt)_2$/*sec*-$BuOP(O)(OEt)_2$. [h] *sec*-$PentOP(O)(OEt)_2$/*sec*-BuO(*sec*-PentO)P(O)OEt. [i] *sec*-BuO(*sec*-PentO)P(O)OEt/$(sec\text{-BuO})_2P(O)OEt$. [j] *sec*-BuO(*sec*-PentO)-P(O)OEt/*sec*-$PentOP(O)(OBu\text{-}sec)_2$. [k] Based on consumed phosphite.

tion of tetraalkoxyphosphoranyl radicals shown in Scheme I. A single example is shown in each case. Designations ea, ee, etc. help one to trace the ligands in the rearrangement, but are not intended to designate any precise physical rearrangement mechanism. For example, as has been pointed out,[7] both the Berry pseudorotation and turnstile mechanisms fall under process M_1. Note that in all but M_3 there is an apical–equatorial exchange of alkoxy groups.

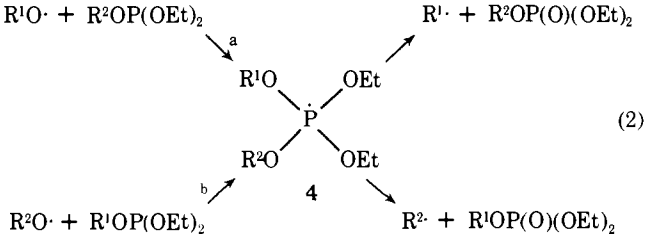
In the present study we have attempted to answer the following questions concerning the processes of eq 1:

(1) In the formation of **1** (**2**), does the attacking RO· enter the TBP in a configurationally selective fashion, i.e., preferentially equatorial or apical?

(2) Is there a configurational preference for β scission; i.e., is it more rapid for a given RO at the apical than at the equatorial position or vice versa?

(3) Is there a permutational process which exchanges alkoxy groups between apical and equatorial positions at a rate greater than or in competition with β scission?

Our approach has been to generate a series of phosphoranyl radicals (**4**) by two different pathways (a and b of eq 2). The systems studied were designed such that at least two



(2)

competitive β-scission processes were available to each intermediate to give two (or more) phosphates. The ratio of product phosphates was then determined for each reaction system to show whether or not that ratio was a function of the mode of formation of presumed tetraalkoxy radical intermediate. Obviously, only possible configurational preferences of the type suggested in questions 1 and 2 above could result in phosphate ratios dependent on the path of formation of **4**. Rapid permutation of alkoxys between equatorial and apical position (question 3 above) would result in loss of "memory" to the system and convergence of phosphate ratios.

On the basis of our studies, we conclude that both processes a and b of eq 1 are configurationally selective and that no apical–equatorial permutation process more rapid than β scission is generally available to the *acyclic* tetraalkoxyphosphoranyl radicals of the type investigated.

Results

In Table I are recorded results of studies of ten different reactions of alkoxy radicals with trialkyl phosphites. Included are four pairs of reactions of the type illustrated for the general case of eq 2. In addition, case 11 is a reaction in which the intermediate phosphoranyl radical of cases 9 and 10 is formed in a third way. *These results show that, for a given pair of reactions involving a "common" intermediate, the product phosphate ratio is in fact dependent on the mode of formation of that intermediate.* Thus, e.g., for case 1, the ratio 1.15 is far outside of experimental error of that for case 2, 0.80. The same four alkoxy groups would be attached to phosphorus in the intermediate in both instances.

Product analyses were done by GLC. Internally standardized sensitivity plots were made for each phosphate to determine yields. But for increased accuracy, phosphate ratios were determined directly from plots of area ratio vs. mole ratio for the particular phosphates in question. Generally, six to eight points were used in each plot, and results of several injections of each mixture were averaged. Plots showed correlation coefficients of better than 0.99 and included the origin.

One notes from Table I that a given alkoxy radical always transfers its oxygen (undergoes β scission) a greater percentage of the time when it is the *attacking* radical than when it is attached to phosphorus in the phosphite. Because of the possibility that this might be an artifact of the method resulting from the presence of oxidizing impurities in the hyponitrite preparations, nearly all reactions were carried out with two or more different hyponitrite preparations, the presumption being that the oxidizing impurity would vary

Table II. Effect of Added Phosphite on the Rate of Thermal Decomposition of Diethyl Hyponitrite at 65 ± 0.01 °C[a]

EtON=NOEt[b]	*sec*-BuOP(OEt)$_2$[b]	$k \times 10^4$, s^{-1}	$t_{1/2}$, min
1.0		4.29 ± 0.23[c]	27.0 ± 1.5[c]
1.0	0.50	4.39 ± 0.25	26.4 ± 1.6
1.0	1.2	4.54 ± 0.10	25.5 ± 0.6
1.0	1.9	4.59 ± 0.10	25.1 ± 1.0

[a] In degassed isooctane. [b] Molar concentrations. [c] Error limits from linear regression analyses, 95% confidence level; correlation coefficients 0.998 or greater.

in amount from one preparation to another. The concentrations of phosphite and hyponitrite were also varied since the oxidative side reaction would be bimolecular. No effect on phosphate results was seen as a result of either variation.

Along these same lines, it seemed possible to us also that decomposition of $(EtO)_2N_2$ might yield some EtOOEt as the *tert*-butyl hyponitrite is known[8] to give di-*tert*-butyl peroxide (about 10%). Decomposition of the $(EtO)_2N_2$ at 65 °C in degassed benzene failed to give detectable peroxide under GLC conditions such that it would have been seen. Further, a control reaction in which EtOOEt and *sec*-BuOP(OEt)$_2$ were mixed together for times and conditions resembling the thermal reactions failed to produce phosphate.[9] This control is assumed to exclude such a possibility with the other hyponitrites as well.

We were also concerned that the phosphate ratios might be influenced by an ill-defined sort of bimolecular attack of phosphite on hyponitrite. This too should have shown an effect of changing reactant concentrations. Further, we determined the effect of added triethyl phosphite on the rate constant for decomposition of diethyl hyponitrite at 65 °C at the concentrations of reactants used in the reactions of Table I. As one may note in Table II, the apparent first-order rate constants with or without phosphite are all within experimental error of each other.

To check product stability to reaction conditions, phosphates in quantities of the order 30–200% of the final phosphate formed were added before the reaction in cases 9, 11, and 12. Phosphate ratios were also checked as a function of extent of conversion of starting phosphite. Neither control showed change in ratios.

For similar reasons we also ran certain of the reactions to varying levels of completion with no effect on product ratios. Unreacted phosphite was also examined at 30–60% reaction and showed no alkoxy exchange. Thus, e.g., no *sec*-BuOP(OEt)$_2$ was detected in the reaction of *sec*-BuO· with $(EtO)_3P$. This is evidence for the *irreversibility of phosphoranyl radical formation* on alkoxy radical attack. We reported similar evidence for this conclusion earlier.[10]

Finally, for the reaction system involving the formation of the potential intermediate *sec*-BuOP(OEt)$_3$, phosphate ratios were determined using first the hyponitrites as EtO· and *sec*-BuO· sources and then the corresponding peroxides, EtOOEt and *sec*-BuOOBu-*sec*. Comparisons of cases 3 and 4 with 5 and 6 of Table I show that the two ethoxy radical sources give results with excellent agreement. Those with *sec*-BuO· are very nearly within experimental error of each other. Considering the difference in temperatures employed, we consider this agreement to be satisfactory. An expanded version of cases 3–6 is found in Table III. In addition to showing the relatively independent nature of the results with respect to the source of alkoxy radical and whether it is thermally or photolytically generated, the lack of effect of solvent on reaction ratios can also be noted. Hyponitrites are decomposed both thermally at 65 °C and by ultraviolet light through Pyrex or Vycor at 16 °C. It can be noted that the agreement between results obtained on reaction of $(EtO)_3P$ with *sec*-BuO· from the two sources is somewhat improved over the averaged results in Table I when photolysis with hyponitrite at 16 °C is compared with photolysis of the peroxide. The possibility that peroxide might react independently with phosphite by the known biphilic route established by Denney[9] was ruled out under our conditions by appropriate control reactions (vide supra).

Table III. Effects of Alkoxy Radical Source, Method of Generation, and Solvent Change on Phosphite Ratios

Reactants	Conditions	Solvent	$(EtO)_3P(O)$/ *sec*-BuOP(O)(OEt)$_2$	% yield[b]
sec-BuOP(OEt)$_2$, $(EtO)_2N_2$	65 °C	C_6H_6	0.71 ± 0.04[a] (2)	91, 94
sec-BuOP(OEt)$_2$, $(EtO)_2N_2$	65 °C	*n*-Hexane	0.76 ± 0.02 (3)	92–93
sec-BuOP(OEt)$_2$, $(EtO)_2N_2$	*hν*, 16 °C	*n*-Hexane	0.75 ± 0.01 (3)	88–90
sec-BuOP(OEt)$_2$, $(EtO)_2$	*hν*, 16 °C	*n*-Hexane	0.79 ± 0.01 (7)	89–92
$(EtO)_3P$, (*sec*-BuO)$_2N_2$	65 °C	C_6H_6	1.09 ± 0.04 (4)	83–90
	65 °C	Toluene	1.05	88
	65 °C	Cyclohexane	1.04	91
	hν, 16 °C	*n*-Hexane	1.03 ± 0.02 (2)	89,91
$(EtO)_3P$, (*sec*-BuO)$_2$	*hν*, 16 °C	*n*-Hexane	0.96 ± 0.01 (4)	80–90
	hν, 16 °C	C_6H_6	0.96 ± 0.01 (6)	80–90

[a] Average errors; number of replications in parentheses. [b] Based on phosphite consumed.

Discussion

Clearly the results of these studies demand, in terms of eq 2, an explanation consistent with the memory effect observed. This effect rules out: (1) a configuration, e.g., tetrahedral, for the phosphoranyl radical intermediate in which all alkoxys are configurationally equivalent; (2) a configurationally random introduction of attacking alkoxy radical into apical and equatorial positions of trigonal-bipyramidal intermediate **2**; (3) a permutational isomerization which exchanges alkoxy substituents between apical and equatorial positions at a rate faster than β scission; (4) accidentally equal reactivity of a given alkoxy group in both equatorial and apical positions.

Let us first consider the benzyloxy radical reactions, the pair constituted by cases 1 and 2. In each instance two phosphates are formed: *p*-$CH_3C_6H_4CH_2OP(O)(OEt)_2$ (**5**) and $C_6H_5CH_2OP(O)(OEt)_2$ (**6**). (The free radical nature of these processes is strongly indicated by the high yields of various bibenzyl coupling products formed in statistically random proportions, i.e.: $C_6H_5CH_2CH_2C_6H_5$, 26%; *p*-$CH_3C_6H_4CH_2CH_2C_6H_5$, 49%; and *p*-$CH_3C_6H_4CH_2CH_2C_6H_4CH_3$-*p*, 25%.) It is important to note that, as expressed in eq 3 and 4, *the ratios of phosphates formed by*

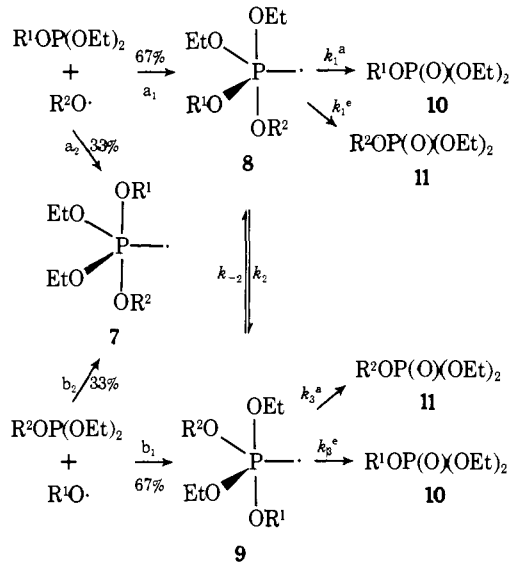
$$C_6H_5CH_2O\cdot + p\text{-}CH_3C_6H_4CH_2OP(OEt)_2 \longrightarrow \mathbf{5} + \mathbf{6} \quad (3)$$
(ratio **5**/**6** = 1.15 ± 0.02)

$$p\text{-}CH_3C_6H_4CH_2O\cdot + C_6H_5CH_2OP(OEt)_2 \longrightarrow \mathbf{5} + \mathbf{6} \quad (4)$$
(ratio **6**/**5** = 1.25 ± 0.03)

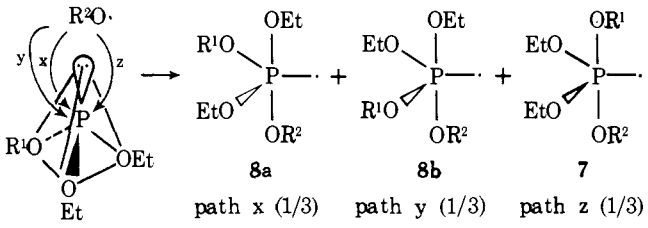
the two pathways are very nearly the inverse of each other within experimental error. This fact allows two possible models based on Scheme II to be set forth. In both, the phosphite is assumed pyramidal. Stereochemical studies of

alkoxy radical oxidations of trivalent organophosphorus derivatives have been shown by us[11] to be stereochemically retentive about phosphorus, as is consistent with initial attack by RO· toward the lone pair of phosphorus. Random attack on the three pyramidal faces (which include the lone pair at one apex) via path a gives intermediate **7** 33% of the time, and 67% of the time yields **8.** (**8a** and **8b** are mirror images. Only **8b** is shown in Scheme II.) In identical fashion path b

Scheme II



gives **7** and **9** 33% and 67% of the time. Such attacks are very fast[3g] and likely to be controlled by statistical factors rather than the small steric differences presented by different alkoxys.[11c]



In model 1 it is assumed that the rate of β scission is much greater than that for the sort of pairwise permutational isomerism shown (which corresponds precisely to a Musher M_1 process), that is $k_1 \gg k_2$ and $k_3 \gg k_{-2}$, and β scission occurs both apical and equatorial. If one takes the product ratios in eq 3 and 4 to be actually within experimental error the inverse of each other, with **5/6** of eq 3 1.20 and **6/5** of eq 4 also 1.20, then it is very easy to show that these ratios would arise if the ratio of rate constants for β scission from the apical and equatorial positions, k_β^a/k_β^e, are 1.3 for both **8** and **9,** and R^1 and R^2 are lost with equal ease from **7.** This would be the case were the β scission rate unaffected by the presence of the p-CH_3 (which serves then as a label) and, thus, $k_1^a = k_3^a = k_\beta^a$ and $k_1^e = k_3^e = k_\beta^e$. In fact, in this model, the not-quite-identical experimental values of the **5/6** and **6/5** ratios of eq 3 and 4 could reflect a small substituent effect on the β scissions. Obviously, to the extent that the introduction of the attacking alkoxy group apical is only configurationally *selective* rather than specific, then the ratio k_β^a/k_β^e would be increased.

An important alternative, model 2, is also based on Scheme II. In this treatment permutational isomerizations **8** → **9** and **9** → **8** occur at rates comparable and competitive with a β scission which is exclusively apical (i.e., k_1, $k_3 \simeq k_2$, k_{-2}; and $k_\beta^a \gg k_\beta^e$). (Since via path a or b of Scheme II more oxygen transfer results from the incoming benzyloxy radical than from the one already attached to phosphorus, equatorial β cleavage cannot be faster than that apical if the attacking RO· is introduced apically.) Radical **8** can give only **10** and **9** only **11.** A steady-state kinetic analysis for path a based on the concentration of **9** gives eq 5. (An identical treatment based on **8** can be done

$$d[\mathbf{10}]/d[\mathbf{11}] = k_1^a(k_{-2} + k_3^a)dt/k_2k_3^a dt \qquad (5)$$

for path b.) If, as we have assumed, β scission is essentially unaffected by the methyl label, then again $k_1^a = k_3^a = k_\beta^a$. It is also reasonable since two benzyloxys are interchanged, that $k_2 = k_{-2}$. With these substitutions and integration, eq 5 gives eq 6. If 67% of reaction 3 (which gives **5/6** = **10/11** = 1.2) proceeds via path a, then the ratio **5/6** (**10/11**) formed via intermediates **8** and **9** is 1.3. From (6) it then

$$\mathbf{10/11} = (k_{-2} + k_3^a)/k_2 = 1 + k_\beta^a/k_2 \qquad (6)$$

follows that $k_2 = k_{-2} = 3.3k_1^a = 3.3k_3^a = 3.3k_\beta^a$. Similarly, pathway b gives expression 7 which shows clearly the

$$\mathbf{11/10} = \frac{k_3^a(k_1^a + k_2)}{k_{-2}k_1^a} = 1 + k_\beta^a/k_2 \qquad (7)$$

exact inverse relationship of **10/11** by the two pathways. Thus, the above results are readily explained if the permutational isomerizations **8** → **9** and **9** → **8** are about three times as rapid as β scission from the apical position.

A choice between these two models can be made by lengthening the lifetimes of intermediates **8** and **9.** ESR measurements show that, at 20 °C, the rate of β scission to give t-Bu· is at least 11–20 times that for formation of a secondary alkyl radical (i-Pr· or c-C_5H_9·) by β scission.[3g] Our own chemical studies of reaction of $PhCH_2O$· with t-$BuOP(OEt)_2$ show the β-cleavage rate for $PhCH_2O$ to be at least 10 times that for t-BuO.[12] Therefore, for cases 3–12 the cleavage rate for the most rapidly cleaved group, the *sec*-alkoxy, must be at least 100 times slower than that for a benzyloxy substituent. Under this condition, $k_2 = k_{-2} = 300k_\beta^a$, and scrambling of the alkoxy positions then must precede β cleavage and result in identical **10/11** ratios. (**10/11** in either expression 6 or 7 reduces to $k_1^a k_{-2}/k_3^a k_2$.) Since this is not seen to be the case for the data of Table I, we conclude that *any permutational isomerization mode (M_1, M_2, M_4, M_5) which exchanges apical and equatorial alkoxys is not competitive with β scissions involving benzyloxy groups.*[13] Whether such a permutation has become comparable in rate with the β scissions of primary and secondary alkoxy groups cannot be ascertained. It can be concluded with certainty that in the studies of Table I more oxygen transfer occurs from the entering secondary alkoxy group than from the one already incorporated in the phosphite reactant. This result is *not* consistent with the view[3b,f,i] that β scission happens more rapidly from the equatorial position. To the extent that Scheme II is valid, we conclude that, *at the temperature studied,* $k_\beta^a > k_\beta^e$. We have also concluded from stereochemical studies of such oxidations that an M_1 permutation does not precede β scission.[10]

The above conclusions require first that the values of k_2 and k_{-2} be essentially equal for $PhCH_2O$ and p-$CH_3C_6H_4CH_2O$ substituents on phosphorus, and, second, that the permutation rate does not change greatly with the nature of the alkoxy group; for example, that k_2 for $PhCH_2OP(OEt)_3$ and *sec*-$BuOP(OEt)_3$ be nearly the same. In pentacovalent phosphorus systems in the absence of rings attached to phosphorus, the relative energies and rates of interconversion of various permutamers depend on the elec-

tronic natures of the substituents undergoing exchange between apical and equatorial positions.[6] In our judgement, primary and secondary alkoxy groups are electronically too similar to affect the value of k_2. Very large steric bulk, such as that of a *t*-Bu, appears to affect the energy of a phosphoranyl radical when that large group is apical.[3c] However, a single branching of the alkyl of an alkoxy takes place at a position remote enough to have little steric effect. New data with regard to these assumptions may lead to some revision at a later time, *but the conclusion that none of the phosphoranyls generated in this study have permutation processes more rapid than their β scissions will remain.*

Our results allow an estimation of a lower limit value for $\Delta G^{\ddagger}$ for apical-equatorial ligand permutation processes of tetraalkoxy phosphoranyl radicals. From kinetic studies, the groups of Davies[3g] and of Ingold[3b] have determined E_a and A for the β-scission process of the radical *t*-BuOP·(OEt)$_3$. From their results it is easy to calculate $\Delta G^{\ddagger}$ at 65 °C for this species to be 10.3–11.5 kcal/mol. By comparison, the data of Davies et al.[3f] allow $\Delta G^{\ddagger}$ at 65 °C for (EtO)$_4$P· β scission to be calculated to be 13.0 kcal/mol. No kinetic studies of benzyloxy radical β scissions have been carried out, but our estimate from product studies that this process is at least 10 times as rapid as that for *t*-BuO lets us estimate $\Delta G^{\ddagger}$ for PhCH$_2$O at 8.5–10 kcal/mol or less. For secondary alkoxy radicals a value of $\Delta G^{\ddagger}$ for β scission would be only about 1 kcal/mol less than that for EtO, based on the relative scission rates, and thus about 12 kcal/mol. Earlier in this paper we concluded that permutation processes are not even competitive with β scissions of benzyloxys. Furthermore, it is seen that permutation processes cannot be more than competitive with the rates of β scissions of ethoxy and *sec*-butoxy groups with $\Delta G^{\ddagger}$ 12–13 kcal/mol. This establishes *a lower limit value of $\Delta G^{\ddagger}$ for apical-equatorial exchanges in these radicals of 10–12 kcal/mol.* This range is in agreement with that we reported earlier based on stereochemical studies in *cyclic* phosphoranyl radicals.[11b]

If, in fact, the attacking alkoxy group enters the phosphoranyl radical intermediate in both apical and equatorial positions and/or only selectively favors the former,[13] then an even *slower* permutation process would be required to explain by model 2 the benzyloxy cleavage patterns noted. This would serve to *raise* the lower limit $\Delta G^{\ddagger}$ estimate for apical-equatorial alkoxy exchange.

We are able to derive a set of relative k_β values for EtO and *sec*-alkoxys which predict the oxidation ratios for Table I on the basis of Scheme II and model 1. β scission is assumed to occur at both apical and equatorial positions. The following relative k_β values for various RO in equatorial or apical positions, derived by trial and error, gave the best fit to the data:

EtO (eq) = 1.0
EtO (ap) = 2.1
sec-BuO (eq) = 3.4
sec-BuO (ap) = 4.5
sec-Pent (eq) = 4.4
sec-Pent (ap) = 4.9

On this basis, the experimental values for the reactions of cases 3, 4, and 7–12 are predicted with an average error of 6%. (See Table IV for comparisons of experimental and calculated numbers.)

As an example of this approach consider reactions 8 and 9 which correspond to cases 3 and 4 of Table I. Reaction 8

$$sec\text{-BuO}\cdot + P(OEt)_3 \longrightarrow \underset{\mathbf{12}}{(EtO)_3PO} + \underset{\mathbf{13}}{sec\text{-BuOP(O)(OEt)}_2} \quad (8)$$

Table IV. Comparisons of Experimental and Calculated Product Ratios[a]

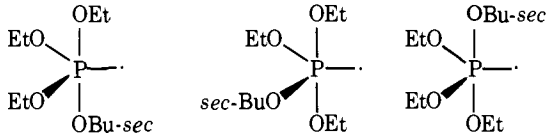
Case	$R^2OP(O)(OEt)_2$/ $R^1OP(O)(OEt)_2$ Exptl	Calcd	$R^2OP(O)(OEt)_2$/ $(R^1O(R^2O)P(O)OEt$ Exptl	Calcd
3	1.1	1.1		
4	0.75	0.80		
7	1.3	1.2		
8	0.95	0.96		
9	1.0	1.0	1.6	1.7
10	0.74	0.81	1.3	1.5
11[a]	0.83	0.82	1.3	1.1
12[a]	1.9	1.8	7.2	6.9

[a] See Table I for actual phosphates formed.

will give intermediate **14** only, whereas reaction 9 would

$$sec\text{-BuOP(OEt)}_2 + EtO\cdot \longrightarrow \mathbf{12} + \mathbf{13} \quad (9)$$

lead to **15** formation two-thirds of the time and **16** the remaining third. For reaction 8 the calculated **12**/**13** ratio is



14 **15** **16**

given by eq 10. For reaction 9 the ratio is calculated by eq

$$\frac{\mathbf{12}}{\mathbf{13}} = \frac{4.5}{(1)(2.1) + (2)(1.0)} = 1.09 \quad (10)$$

11. The experimental values of Table I are 1.07 and 0.75.

$$\frac{\mathbf{12}}{\mathbf{13}} = (0.67)\left[\frac{4.5}{2(2.1) + (1.0)}\right] + (0.33)\left[\frac{4.5}{2(1.0) + (2.1)}\right] = 0.80 \quad (11)$$

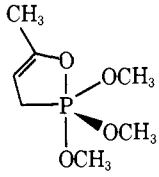
The internal consistency of the results are gratifying in that the relative ease of β scission follows radical stability, and there is a preference in each instance for apical β scission (as had been found for benzyloxy) although the preference is only slight for *sec*-pentoxy. The slower β scissions (EtO groups) are the more selective ones as is reasonable. The increase in apical equatorial selectivity would be even greater in the series benzyloxy, *sec*-alkoxy, ethoxy, if in fact an apical-equatorial permutation process is competitive with β scission. The applicability of the above relative rate constants for β scission to a number of reactions increases our confidence in the reliability of our results.

Earlier we reported[10] that the reaction of ^{14}C-labeled *t*-BuO· with (*t*-BuO)$_3$P displayed no memory effect, the β scissions of the four *tert*-butoxy groups being random. If in (*t*-BuO)$_4$P· k_β^a/k_β^e were 1.3, the memory effect would not have been detectable within the errors limits of the experimental method, ±3%. A recent ESR study of this radical also failed to reveal a memory effect.[3k]

Comparisons with Phosphoranes and Other Phosphoranyl Radical Studies. Although no direct measurements have been made of permutation barriers in noncyclic pentaalkoxyphosphoranes, it seems most certain that they should be several kilocalories/mole less than 10. For example, the exchange of identical substituents, fluorines, between apical and equatorial positions in PF_5 must have $\Delta G^{\ddagger}$ below 5 kcal/mol.[14] The barrier to methoxy exchange in **17**, which likely requires that the ring CH_2 be placed in the electronically unfavorable apical position, is 10 kcal/mol.[15] That for the oxy analogue, **18**, must be considerably lower. No barrier for PhP(OEt)$_4$ has been measured since the alkoxys remain equivalent at the lowest temperatures measured (−65

°C).[16] Compared with pentaalkoxyphosphoranes the barriers to apical-equatorial alkoxy permutations in $(RO)_4P\cdot$ are surprisingly high. *The idea that phosphoranyl radicals are simply analogues of the well-studied phosphorane counterparts apparently is an oversimplification.*

There is a certain amount of data available from ESR work on phosphoranyl radicals which has been interpreted in terms of fast intramolecular exchange of substituents. Although the possible effects of quantum-mechanical tunneling are not known, $\Delta G^{\ddagger}$ at −75 °C for apical-equatorial hydrogen exchange in t-$BuOPH_3$ has been measured at 5.3



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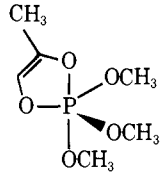

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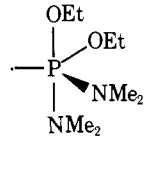

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kcal/mol.[17] Exchange of Me_2N groups in **19** occurs with estimated rate constant of 10^8 s^{-1} at −110 °C.[3e] Processes of similar rapidity seem to occur with various phosphoranyls in which phosphorus is part of a single ring attached apical-equatorial. For the cyclic systems, an M_4-like permutation is suggested.[3e] However, the species $\dot{P}H_4$[18] and $\dot{P}F_4$[19] show no evidence of substituent exchange (in spite of earlier reports[20] to that effect), at least at low temperatures, nor does PCl_4.[21] However, fluorine exchange has been observed most recently with $RO\dot{P}F_3$ with $\Delta G^{\ddagger}$ about 7 kcal/mol.[22] The effects of a ring on barriers to exchange are not known nor is it easy to predict the relative ease of intramolecular exchange of fluorines vs. alkoxy groups. Studies of cyclic systems of the type reported here for acyclic $(RO)_4P\cdot$ are in progress in our laboratory. Our previously published stereochemical work[11b] on β scission cannot rule out an M_4 (or M_5) exchange although an M_1 process is excluded.

It has been called to our attention[23] that phosphoranyl radicals are Jahn-Teller systems, and their energies are expected to be more sensitive than those of PX_5 to distortions from preferred geometry. Theoretical calculations comparing energies of trigonal bipyramidal and square pyramidal (apical odd electron) structures for $\dot{P}H_4$[24] (ab initio methods), $\dot{P}O_4^{4-}$ [23a] (extended Hückel method), and $\dot{P}F_4$[25] (CNDO/2) all suggest that a *physical mechanism* of pairwise apical-equatorial exchange for phosphoranyl radicals involving a square pyramidal intermediate or transition state (Berry pseudorotation) will involve *more energy* than it would for analogous pentacovalent systems, e.g., PH_5 or PF_5. Whether other pathways and operational modes of permutation may be of relatively lower energy in phosphoranyl radical systems will be of interest to determine.

Experimental Section

Many of the phosphites were commercially available or known compounds. Others were synthesized by standard methods and, if new compounds, subjected to quantitative elemental microanalysis at Galbraith Laboratories, Knoxville, Tenn., or Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Melting points are uncorrected.

Dibenzyl hyponitrite was prepared according to the method of Partington and Shah,[26] mp 47–48 °C, lit.[26] 48–49 °C. Similarly di-(p-methylbenzyl) hyponitrite was prepared, mp 67–69 °C, from ether. Its decomposition products in degassed benzene solution were shown by GLC to be p-methylbenzyl alcohol and p-methylbenzaldehyde. The procedure of Denney et al.[27] was utilized to prepare diethyl peroxide. The procedures of Partington and Shah also were followed to give the other hyponitrites. These materials were colorless oils. The only means of their purification consisted of pumping on them at very high vacuum at room temperature in a vessel containing P_4O_{10}. The ethyl compound was especially easy to check for purity by ^1H NMR which indicated it to be 90–95% or better in each preparation. ^1H NMR spectra for the *sec*-butyl and *sec*-pentyl compounds showed the absence of major impurities. Di-*sec*-butyl peroxide was prepared by the method of Welch, Williams, and Mosher, 10% yield.[28]

The phosphites used were prepared in mostly routine fashion when not available. Oxidation with N_2O_4 gave the required phosphates. Treatment with S_8 yielded the thiophosphates. All were purified to levels <99% by distillation or, if required, by preparative GLC. *sec*-$BuOP(OEt)_2$ and *sec*-$PentOP(OEt)_2$ were prepared from the alcohol and $(EtO)_2PCl$ in anhydrous ether. The benzyl phosphites were made in one-pot reactions in which the benzyl or p-methylbenzyl alcohol was added dropwise to a solution of PCl_3 and Et_3N in ether cooled to −30 °C. Following the first addition, a second portion of Et_3N was added and then ethanol. Similar procedures afforded EtO(*sec*-BuO)POPent-*sec* and (*sec*-$BuO)_2POEt$. The two new phosphites used were subjected to elemental analysis as the phosphate. These were: p-$MeC_6H_4CH_2OP(O)(OEt)_2$ (Anal. Calcd for $C_{12}H_{19}O_4P$: C, 55.81; H, 7.42; P, 11.99. Found: C, 55.89; H, 7.50; P, 11.81) and EtO(*sec*-BuO)P(O)OPent-*sec* (Anal. Calcd for $C_{11}H_{25}O_4P$: C, 52.37; H, 9.99; P, 12.27. Found: C, 52.21; H, 9.96; P, 11.92).

Reactions. All reactions were carried out in glass tubes which had been carefully washed with cleaning solution, ammonium hydroxide, five rinses of distilled water, and then acetone before being oven dried. The tubes were fitted with rubber serum caps and flushed with pure nitrogen. Phosphite and hyponitrite or peroxide were weighed into a volumetric flask, followed by addition of solvent to the dilution mark. These solutions were transferred by syringe methods to the serum-capped tubes and then degassed several times by the freeze–thaw method on a high-vacuum line before sealing at 10^{-4}–10^{-5} mm. The thermal reactions were carried out in a bath at 65 ± 0.01 °C for 5–10 half-life initiator decomposition times. Unreacted phosphite was converted to the thio derivative by addition of sulfur following reaction. An internal standard was then weighed into each tube and GLC analysis was carried out on an F & M Model 810 thermal conductivity detector instrument. Details of the sensitivity calibrations and GLC analysis procedures are given in the Results section.

Photoreactions were carried out in Vycor or Pyrex tubes (reaction unaffected by choice) at 16 ± 1 °C. The tubes were strapped to the outside of a water-cooled quartz thimble into which was inserted a Hanovia 200 or 450 W medium-pressure mercury-vapor lamp.

Kinetics of $(EtO)_2N_2$ Thermal Decomposition. About 2 ml of an isooctane solution of $(EtO)_2N_2$ (1.0 M) and diethyl *sec*-butyl phosphite (0.0, 0.5, 1.0, and 2.0 M levels) was placed in a tube fitted with a rubber septum. The solution was then flushed with pure nitrogen and placed in a bath at 65 ± 0.01 °C. The tube was sampled every 7–8 min over a 2-h period by use of a 100-μl Hamilton syringe. Samples taken were diluted appropriately with isooctane so that the uv absorbance maximum at 223 nm could be measured. First-order rate constants were calculated from plots of $\ln (A_0 - A_\infty)/(A_t - A_\infty)$ vs. time, where A_0, A_t, and A_∞ represent absorbances at start of reaction, time t, and infinite time (10 half-lives). Linear regression analysis gave the rate constants and errors (95% confidence level) of Table II.

Acknowledgment. This research was supported by research grants from the National Science Foundation (GP-36637X) and the National Cancer Institute of the Public Health Service (CA-11045).

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(12) T. B. Min, unpublished results from this laboratory.
(13) Given the case that k_β^a be only greater than k_β^e, the conclusion remains the same. Under this condition, $k_2(k_{-2})$ would be less than 3.3 k_β^a; but the increase in lifetimes of **8** and **9** would still result in equilibration and memory loss.
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Some Caged Polycyclic Phosphoranes[1]

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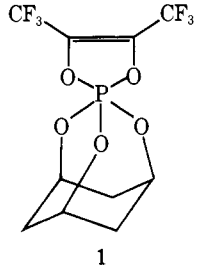
Abstract: A series of caged polycyclic thiooxyphosphoranes and oxyphosphoranes has been prepared by allowing the dithietene **6**, the dioxetane **14**, and hexafluorobiacetyl to react with bicyclic phosphites. Those products which contain only six-membered rings in the bicyclic moiety have NMR spectra which show that, over the temperature range investigated, there is a rapid intramolecular motion which renders the nuclei under investigation equivalent. On the other hand, introduction of one or more five-membered rings into the bicyclic moiety leads to an inhibition of this intramolecular process, and activation energies of 12–19 kcal/mol are found for these substances. The increase in activation energy is probably associated with an increase in strain in the five-membered ring(s) during the intramolecular isomerization.

During the past several years Ramirez, Ugi, and their coworkers have prepared a number of caged polycyclic oxyphosphoranes by condensation of phosphites with hexafluoroacetone and hexafluorobiacetyl.[2] Representative structures are **1–3.** These substances' structures have been studied by



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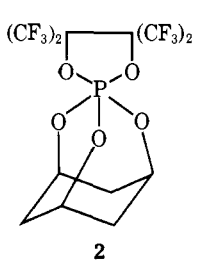

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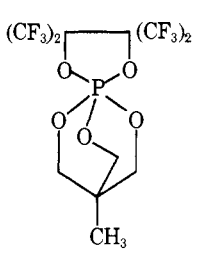

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variable-temperature NMR measurements. The data show that the fluorines of the trifluoromethyl groups of **1** are equivalent over all the temperatures investigated. The same is true for compounds **2** and **3.** Similarly, the hydrogens on the carbons bonded to oxygen of **1** are equivalent over the temperature range studied. Once again the same was found to be true for **2** and **3.** No structure, trigonal bipyramid or square pyramid, can account for the NMR data, and it has been concluded by Ramirez and Ugi that there is a low-energy intramolecular exchange pathway for interconversion of trigonal-bipyramidal structures which renders the various nuclei equivalent. An alternative ionization–recombination mechanism has been considered and rejected on the basis of the lack of change of the ^{31}P NMR chemical shifts with increasing polarity of solvent. It has been shown in the past that an ionization–recombination equilibrium does in general show changes in ^{31}P NMR chemical shifts with changes in solvent. More recently[2] it has been reported that FCCOP coupling has now been observed for compounds **1** and **2.** This observation removes any kind of dissociation–recombination mechanism as a means of accounting for the equivalent fluorines. Ramirez and Ugi have considered various intramolecular pathways by