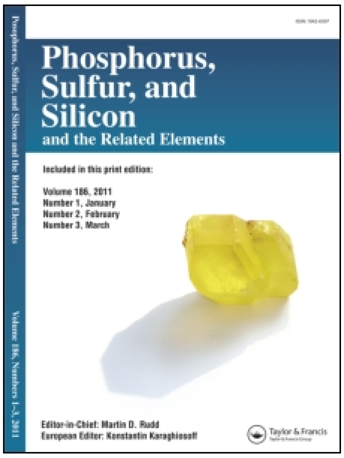

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PHOSPHORANYL RADICALS

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PHOSPHORANYL RADICALS†

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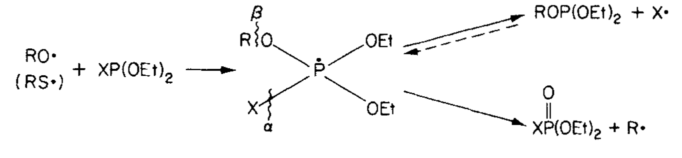
A summary of findings on factors which determine the reactivity of a radical (Z·) towards trivalent phosphorus (PX_3) is given along with a brief discussion of the competition between α- and β-scission alternatives for the phosphoranyl radicals ($Z\dot{P}X_3$) which are probable intermediates in these reactions. This is followed by a detailed discussion of certain stereochemical and chemical labelling studies of the configurations of phosphoranyl radicals and of the possible permutational isomerizations which they could undergo. It is concluded that although certain of the properties of truly pentacovalent phosphorus compounds are displayed by phosphoranyl radicals, pairwise permutations occur relatively slowly with the tetraalkoxy species. Further it is postulated that the attacking radical (Z·) is introduced into the trigonal bipyramidal intermediate ($Z\dot{P}X_3$) with configurational selectivity.
radical formation.

INTRODUCTION

Phosphoranyl radicals, $Z_4P\cdot$, have been postulated as intermediates to explain certain reactions of free radicals with trivalent phosphorus derivatives.[1] This is depicted in general by reaction (1). Phosphorus-X bond cleavage (α-scission) gives phosphite product, and the process is substitution (reaction (2)). Oxidation (reaction (3)) results when carbon-oxygen cleavage (β-scission) occurs to yield oxide, $XP(O)(OEt)_2$. In instances in which bond formation between a radical X· and phosphorus (reverse of the α-scission process) is followed by rapid β-scission, the result is the free-radical equivalent of an Arbuzov reaction (reaction (4)). Although phosphoranyl radicals undergo other reactions, these are the most important in terms of observable chemistry and the formation of isolable products.



(1)

Substitution: $RO\cdot + XP(OEt)_2 \rightarrow ROP(OEt)_2 + X\cdot$ (2)
Oxidation: $RO\cdot + XP(OEt)_2 \rightarrow R\cdot + XP(O)(OEt)_2$ (3)
Free-radical Arbuzov: $X\cdot + ROPOEt)_2 \rightarrow XP(O)(OEt)_2 + R\cdot$ (4)

Evidence consistent with the presence of phosphoranyl radicals in processes of the above type has been derived from esr studies[2] of reactions of thiyl, alkoxy, and alkyl radicals with trivalent phosphorus compounds including cyclic ones. The structure normally assigned to these intermediates is a trigonal bipyramidal one, 1. The substituents of species studied to date have included[2] a variety of combinations of halogen, RS, RO, alkyl, aryl, and dimethylamino. The assignment of the equatorial position to the odd electron in 1 reflects the high 3*s* spin density on phosphorus as shown by isotropic hyperfine splittings to phosphorus (a_P) in the approximate range 650-1350 G. (For an electron in the 3*s* orbital of atomic phosphorus, a_P is calculated to be 3630 G.[3]) An alternative structure for phosphoranyl radicals is 2 which features a Rundle[4] type of bonding scheme. In 2 two electrons are in an apical 3-centered bonding MO, and the odd electron is distributed over the apical ligands in a non-bonding molecular orbital. A similar bonding description has recently been proposed[5] for $POCl_3^-$ on the basis of experimentally determined anisotropic hyperfine splittings. It is likely that the true bonding picture for phosphoranyl radicals is very much substituent-dependent and in

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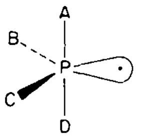
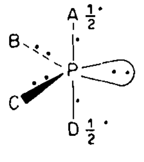
many cases intermediate between the two extremes represented by **1** and **2**. Throughout this paper I will use structures analogous to **1** since we are concerned primarily with geometries, and both **1** and **2** are trigonal bipyramidal.



1



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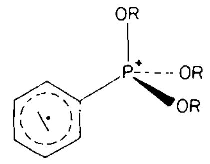


3

Very recently esr evidence has been presented[6] which suggests that phosphoranyl radicals with one or more aryl groups attached directly to phosphorus have tetrahedral geometries, as depicted in **3**, with the odd electron in the π-system. This finding appears to be a very important one.

Esr evidence for the presence of phosphoranyl radicals has been reinforced by recent ^{31}P CIDNP studies.[7] In addition, these investigations give detailed information concerning the reaction processes which follow phosphoranyl radical formations and should prove most valuable aids in mechanistic study. The use of ^{31}P CIDNP was described by Professor Levin at this Conference.[7f]

Over the past several years, my research group has been seeking answers to the following questions concerning reactions of free radicals, $Z\cdot$, with trivalent compounds, PX_3.

1) To what extent are phosphoranyl radicals truly intermediates in such systems?
2) What factors control the reactivity of a given radical Z towards a compound PX_3?
3) What are the configurations of phosphoranyl radicals?
4) To what extent do the strain and stereoelectronic (polarity) rules found in pentacovalent phosphorus systems apply to $Z\dot{P}X_3$?
5) Do groups enter and leave (α-scission) the presumed trigonal bipyramidal radical and/or undergo β-scission in a stereospecific manner?
6) What factors control whether α- or β-scission will be predominant?
7) Do permutational isomerizations of phosphoranyl radicals compete with α- and β-scissions?

These questions are concerned with three important areas of interest: How are phosphoranyl radicals formed? What are their configurations? How do they react?

In this paper I will deal primarily with questions concerning configuration and its relation to phosphoranyl radical formation and reaction. In stereochemical and configurational work, our approach has been to use what is known concerning truly pentacovalent systems, X_5P, as a reference point against which to test the properties of phosphoranyl radicals. If the odd electron is viewed as a ligand (or phantom ligand) the similarities between the two species X_5P and $X_4P\cdot$ become obvious.

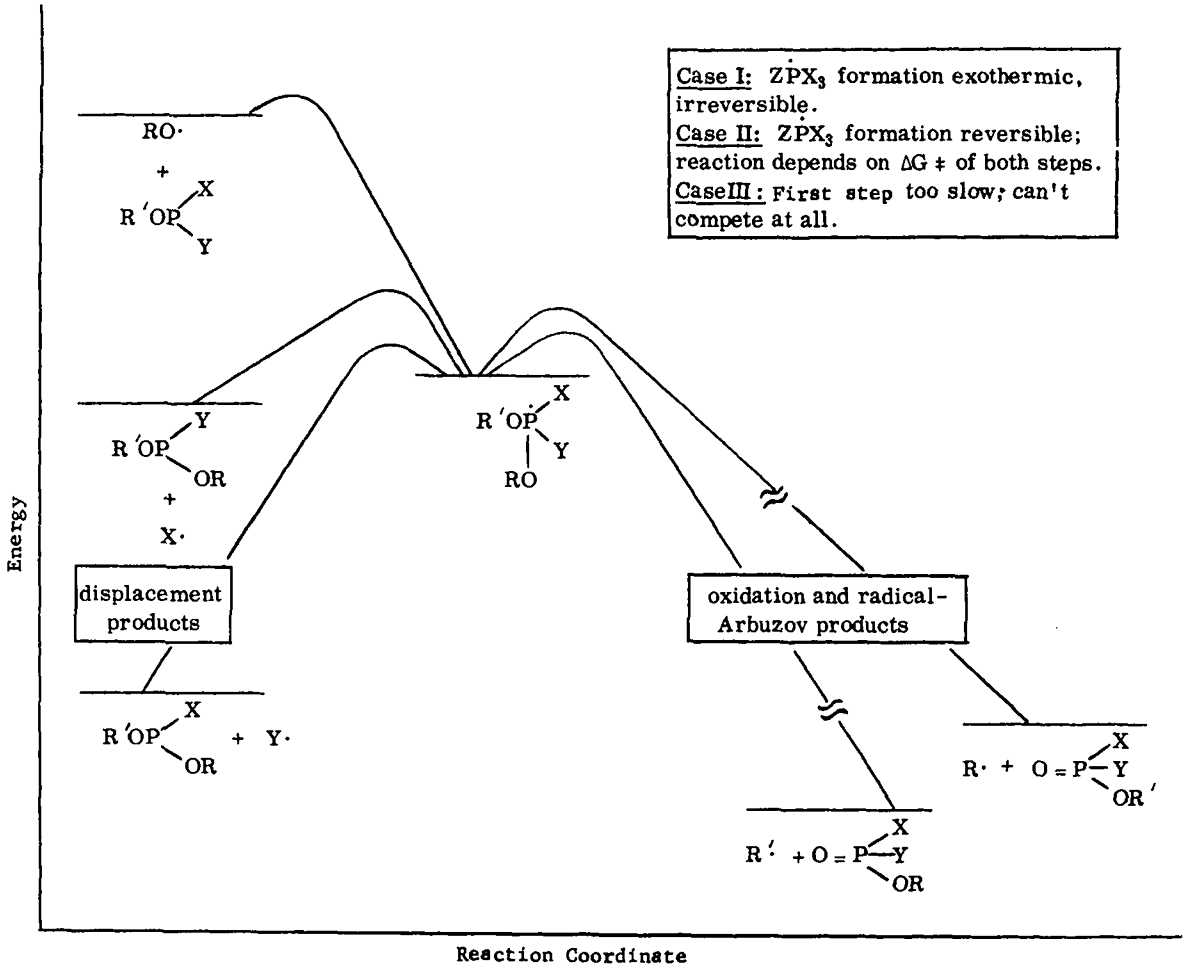
REACTIVITY AND PRODUCT FORMATION

Before discussing in detail our configurational studies, I should like to give a quick summary of wo primarily but not entirely ours, on reactivity and reaction pathways (α- vs. β-scission) in phosphora radical systems. Concerning the reactivity of a given radical $Z\cdot$ towards a potential reactant PX_3, we have concluded[8] that the *strength of the P–Z bond* to be formed in the intermediate $Z\dot{P}X_3$ is of primary importance. Certain *polar* and *steric* factors play a secondary role.

The importance of bond strengths on $Z\dot{P}X_3$ formation is depicted in general terms in Figure 1. Three cases may be distinguished. When a radical which forms a relatively strong bond to phosphorus is the reactant, then the addition step ($Z\dot{P}X_3$ formation) is rapid, exothermic, and rate determining (Case I). The intermediate then undergoes α- or β-scission as determined by the factors outlined below. In Case II the formation of $Z\dot{P}X_3$ is less favorable energetically and therefore reversible. Net product formation requires that the second step

(α- or β-scission) to be relatively rapid. If the P–Z bond to be formed is very weak (Case III), no product results regardless of how fast the second step may be as the intermediate is inaccessible.

From available evidence concerning the competition between α- and β-scission, one concludes[9] that changes in the relative strengths of the bonds undergoing scission in (1) are of greatest importance in determining which product is dominant. For reasons not well understood, phenyl-substituted phosphoranyls are more susceptible to β-scission than they would otherwise be.[20] Table I shows the increase in k_β (rate constant for β-scission) with weakening of the bond to be cleaved. The relative β-scission rates for RO and RS should be compared only within each series. Note that the series of RS, all of which undergo cleavage very rapidly, show less effect of R· stability than does the series of RO.



Case I: $Z\dot{P}X_3$ formation exothermic, irreversible.

Case II: $Z\dot{P}X_3$ formation reversible; reaction depends on $\Delta G^{\ddagger}$ of both steps.

Case III: First step too slow; can't compete at all.

FIGURE 1 Importance of bond strengths on reactivity in phosphoranyl radical reactions.

TABLE I

Approximate relative rates of β-scission for $RO\dot{P}\lessgtr$ and $RS\dot{P}\lessgtr$

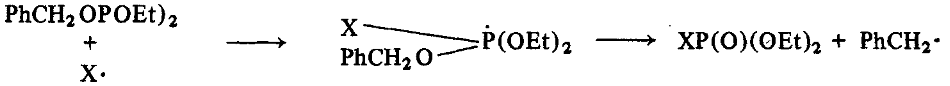
RO	$k_{\text{rel.}}(65^\circ)$	Ref.	RS	$k_{\text{rel.}}(60^\circ)$	Ref.
EtO	1	10	*i*-PrS	1	11
sec-RO	3	10	*t*-BuS	2	11
tert-BuO	$>100^a$	10, 2c	p-$CH_3C_6H_4CH_2S$	6	11
$PhCH_2O$	$>10^3$	10, 2c,d			

[a] Calculated from A and Ea values (Ref. 2d).

Figure 2 depicts the energetics of reaction of RO· with a variety of $XP(OEt)_2$. It can be seen readily that oxidation to give $XP(O)(OEt)_2$ is far more favorable energetically than is displacement of X· (based on average bond strengths[1] for PX_3). Reaction of an alkoxy radical to give the phosphoranyl radical is very fast ($E \cong 2$ kcal/mol[2c]). It is found experimentally[9] that when RO is *t*-BuO, only substitution results for X = Et or any alkyl of the series, X = Et, *i*-Pr, *t*-Bu, and $PhCH_2$ (reaction (5)). However, as the carbon-oxygen bond is weakened, as in reaction (6), oxidation competes with α-scission. The relative amount of α-scission is dependent upon R stability.[9] Because of the increased rate of β-scission when RO = $PhCH_2O$ (Figure 2), several free-radical Arbuzov reactions (7) occur which cannot be observed when RO = *t*-Bu. The isopropyl radical is too unreactive, and no product is found (Case III).[12,13]

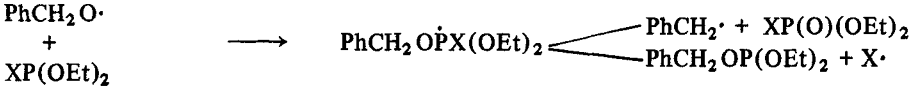
$$t\text{-BuO}\dot{P}R(OEt)_2 \not\longrightarrow t\text{-Bu}\cdot + RP(O)(OEt)_2 \qquad (5)$$

$$PhCH_2O\dot{P}R(OEt)_2 \longrightarrow PhCH_2\cdot + RP(O)(OEt)_2 \qquad (6)$$

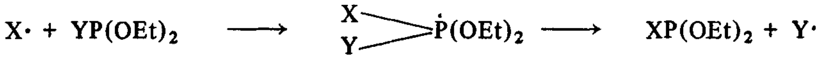


$$PhCH_2OPOEt)_2 + X\cdot \longrightarrow \begin{matrix} X \\ PhCH_2O \end{matrix}\!\!>\dot{P}(OEt)_2 \longrightarrow XP(O)(OEt)_2 + PhCH_2\cdot \qquad (7)$$

(X = PhO·(Ref. 13); Me_2N· (Ref. 13); Et· (Ref. 12))



$$PhCH_2O\cdot + XP(OEt)_2 \longrightarrow PhCH_2O\dot{P}X(OEt)_2 \begin{matrix} \nearrow PhCH_2\cdot + XP(O)(OEt)_2 \\ \searrow PhCH_2OP(OEt)_2 + X\cdot \end{matrix} \qquad (8)$$



$$X\cdot + YP(OEt)_2 \longrightarrow \begin{matrix} X \\ Y \end{matrix}\!\!>\dot{P}(OEt)_2 \longrightarrow XP(OEt)_2 + Y\cdot \qquad (9)$$

For the series of reactions given by (8), and the α/β scission increases with the order of ease of displacement: $PhCH_2\cdot$ > *t*-Bu· > *i*-Pr· > Et· > Me· > $Me_2N\cdot$ > PhO· > RO· . Any radical in the series will displace all of those to its left.[12,13] These examples are illustrative of the effect of relative bond strengths on the α/β scission competition and of the strength of the bond formed to phosphorus on radical reactivity. The phosphorus-oxygen bond is formed very rapidly and irreversibly.[10,14] But when various X add reversibly to phosphorus, either rapid α- or β-scission (Case II, Figure 1) is required for net product formation.

Table II lists measured values of the rate constant, k_p, for irreversible formation of a phosphoranyl radical. With these extremely reactive radicals, low Ea values and large k_ps are the rule. The Ea value for reaction (3) was estimated from the rate constant obtained by competitive kinetic techniques with $(EtO)_3P$ as the reference compound. The assumption was made that the A value determined[2c] for reaction of a *t*-BuO· with $(EtO)_3P$ would apply to reaction with $PhP(OMe)_2$. In reactions (4) and (5), log A is an assumed value for bimolecular reaction. Its use allowed estimations of Ea to be made.

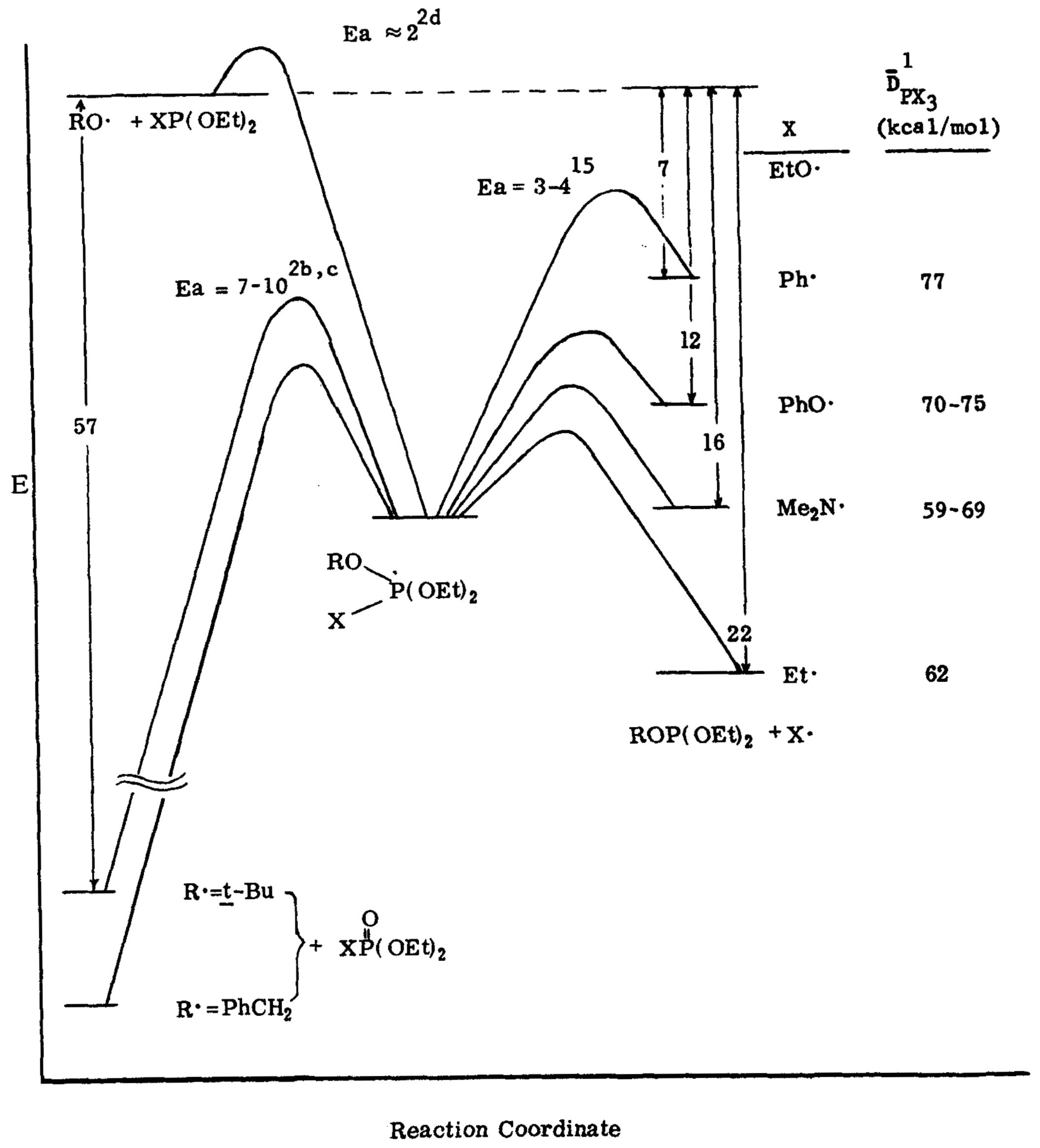


FIGURE 2 Energetics of oxidation, substitution, and free-radical Arbuzov reactions.

Evidence for the minor importance of polar factors on reactivity comes from the failure to find[8] an effect of substituent change on the reactivity towards *t*-BuO· of a series of arylphosphonites (reaction (10)). Similarly, *t*-BuOO· reacts rapidly with a series of PX_3 (reaction (11)) with only minor effects on the rate constant[17] (correlated by Hammett σ^*, equation 12). The range of k_p values at −95° corresponds to a change in Ea of only 1.5 kcal/mol. This result confirms previous auroxidation studies.[18,19] An early study showed the compounds *n*-Bu_3P, $(EtO)_3P$, and Ph_3P to have relative reactivities towards *t*-BuO of 1.2, 1.0, and 0.49 respectively.[16]

TABLE II
Measured values of k_P

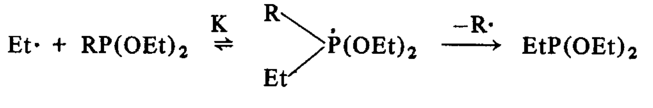
Reaction	Radical	Phosphorus compound	k_P (M^{-1} sec^{-1})	T	Ea	Log A	Ref.
1	t-BuO·	$(EtO)_3P$	2.4×10^8	65	2.24	9.83 [a]	2c
2	t-BuO·	Et_3P	3.0×10^8	65	1.34	9.34 [b]	2i
3	t-BuO·	$PhP(OMe)_2$	3.5×10^8	65	2.0	9.83 [c]	8
4	Ph·	$(MeO)_3P$	4.5×10^6	60	3.6	9 [c]	15
5	n-BuS·	$(EtO)_3P$	2.5×10^8	70	0.9	9 [c]	16

[a] By esr from competition for t=BuO between $(EtO)_3P$ and *cyclo*-C_5H_{10} (k_H) with $\log k_H = 9.0 - 5.2/2.303\ RT$.
[b] By competition with $(EtO)_3P$.
[c] Assumed.

$$t\text{-BuO}\cdot + X{-}C_6H_4P(OEt)_2 \longrightarrow t\text{-Bu}\cdot + X{-}C_6H_4P(O)(OEt)_2 \quad (10)$$

$$t\text{-BuOO}\cdot + PX_3 \longrightarrow t\text{-BuOO}\dot{P}X_3 \longrightarrow t\text{-BuO}\cdot + OPX_3 \quad (11)$$
$$PX_3 = (RO)_3, Br_3P, Cl_3P, Ph_3P, Ph_2PH, Ph_2PMe, Ph_2PCl$$

$$\log k_P = 2.6 - 0.75\ \Sigma\sigma^* \text{ at } -95^\circ \quad (12)$$

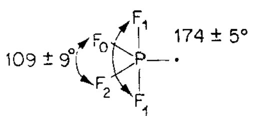

(13)

A very recent unpublished[12] investigation of displacements of alkyl groups by Et· attack at trivalent phosphorus (equation 13) shows that the relative abilities of the alkyl phosphonites to trap Et vary in the order $PhCH_2 > n$-Bu $> i$-Pr $> t$-Bu. We interpret this order to mean that benzyl leaves the intermediate very fast following its otherwise reversible formation. In the other three cases, we propose that the K of reaction (13) is shifted progressively to the left as the result of steric interactions which are not overcome in these instances by increasingly rapid departure of R· . Of course some other step prior to α-scission, such as a required ligand permutation, may be what is affected.[2n]

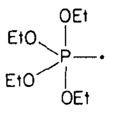
STUDIES OF CONFIGURATION

The structures of radicals **4**-**9** illustrate most of the structural principles presently known concerning phosphoranyl radicals. In **4** two isotropic fluorine splittings are found, the higher value assumed to be from the apical pair. Extended Huckel,[21] valence bond,[21] and CNDO[22] calculations all predict a trigonal bipyramidal lowest energy geometry for $F_4P\cdot$. The angles given are for the extended Huckel and valence bond work of Higuchi.[21] More recent CNDO/2 work of Thomson and Kilcast[22] and that reported by Penkovsky and Gorlov[23] predict a geometry distorted much more towards tetrahedral with $\sphericalangle F_1PF_1$ of about 220°. Radical **6** shows two sets of methyl hydrogens. The pair of equivalent methyls in **7** have nearly the same a_H as the pair in **6** and is presumed to be equatorial in both. This assumption is made on the basis of the stereoelectronic rule which applies to truly pentacovalent phosphorus derivatives.[24,25] In radical **9** the single hydrogen is assumed to be apical, and the large a_H suggests a remarkably high H 1s spin density.

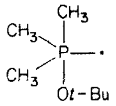
Results of this type form the basis of the assumptions we make in our stereochemical and configuration work: (1) that such intermediates are near trigonal bipyramidal; (2) have a preference for the odd electron to be equatorial; and (3) prefer to have the more electronegative substituents apical. Our approach in the further examination of such systems has been to compare them first to pentacovalent systems, about which a considerable amount is known.



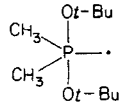
4[2a]
a_P = 1330 G
a_{F_1} = 282 G;
a_{F_2} = 59 G (-135°)



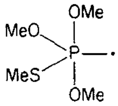
5[2d]
a_P = 884 G



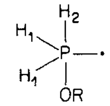
6[2a]
a_P = 619 G
a_{H_1} = 4.6 G
a_{H_2} = 2.8 G



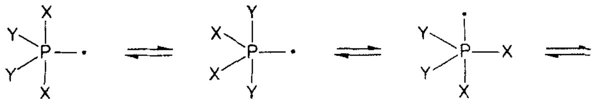
7[2a]
a_P = 715 G
a_H = 2.5 G



8[2e]
a_P = 748 G

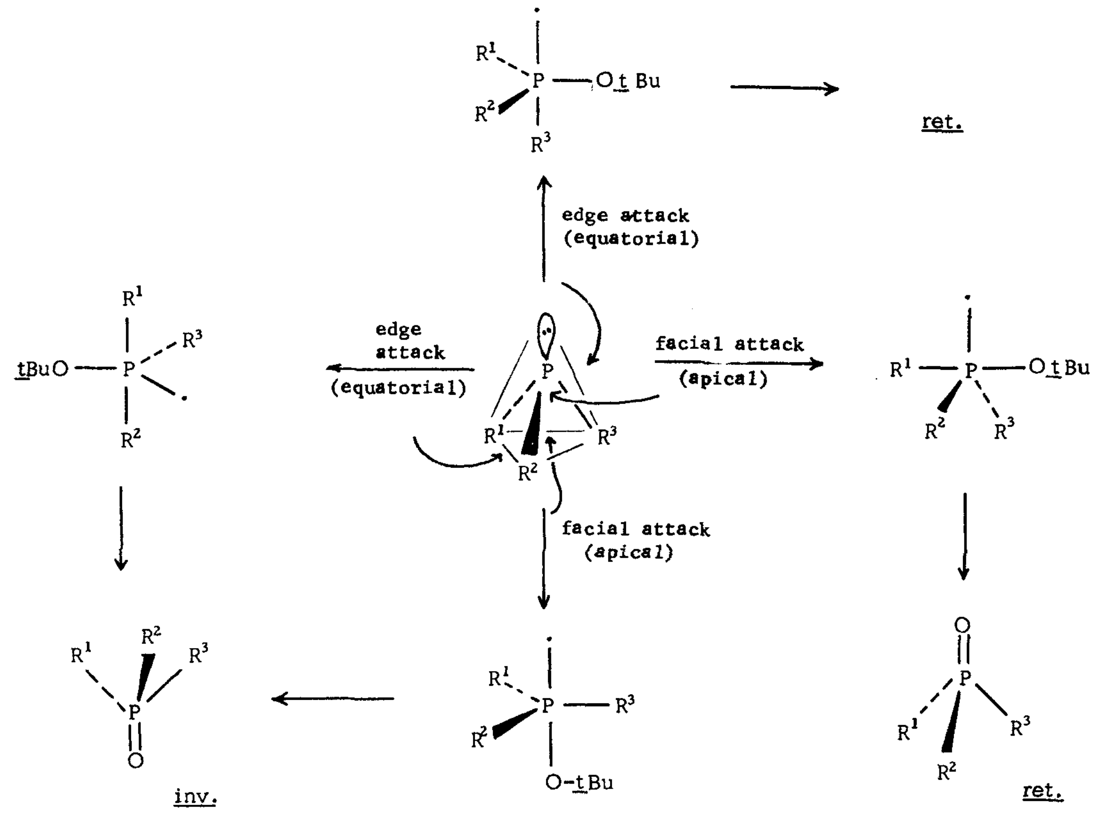


9[2a]
a_P = 627 G
a_{H_1} = 11 G
a_{H_2} = 140 G



etc. (14)

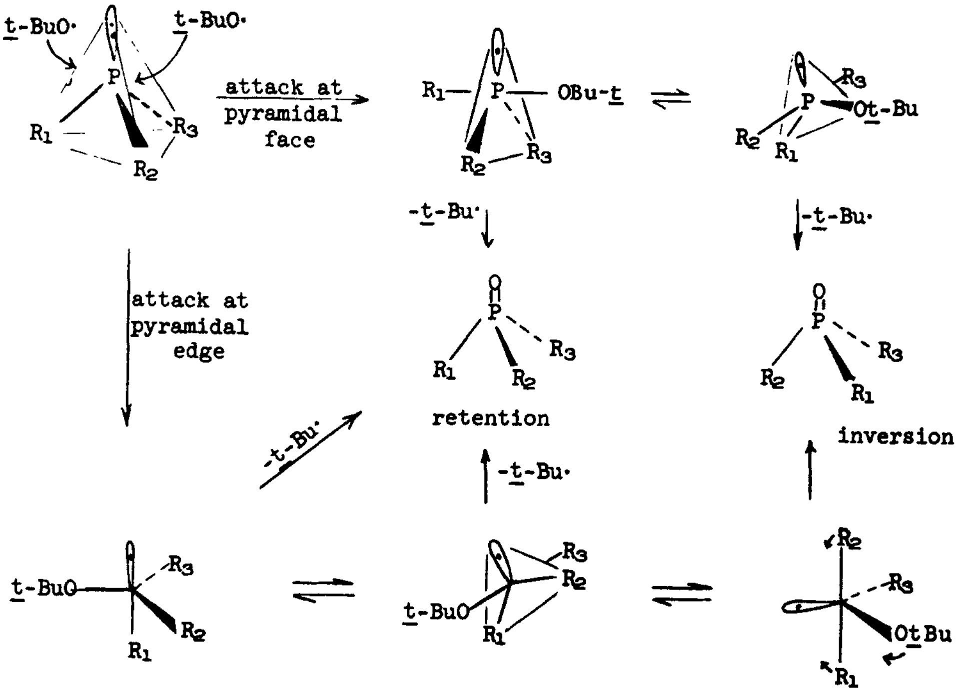
The sort of pairwise permutation (Berry or turnstile mechanisms) widely assumed[25] to be operative in pentacovalent systems is shown for a phosphoranyl radical in (14). In the studies to be discussed in the remainder of this paper, we have been testing the systems to see whether or not permutational process (14) is able to compete kinetically with chemical processes such as α- and β-scission. Of course we are quite aware that other permutational modes[26] may be kinetically favorable in phosphoranyl radical systems. Results will be presented which speak against process (14) being rapid, but this does not mean that *all* permutation processes are relatively slow for phosphoranyl radicals. We have been asking in these investigations several further questions. Do substituents enter and leave the presumed trigonal phosphoranyl species in a configurationally specific manner (apical or equatorial)? Is β-scission preferentially apical or equatorial? Do the strain[25,27] and polarity[24,25] (stereoelectronic) rules affect the *rates of formation* of phosphoranyl radicals of various alternative configurations? Our work on these questions falls into two classes: studies of *stereochemistry* and *chemical labelling* investigations. First we will consider the stereochemical work.



Scheme 1. Effect of mode of attack on stereochemistry of alkoxy-radical oxidation of a chiral phosphine.

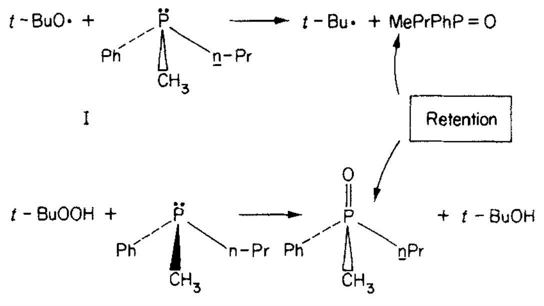
Scheme 1 shows clearly that the stereochemical outcome of the oxidation of a chiral phosphine *via* a phosphoranyl radical intermediate depends on the direction of radical attack. Ten different initial intermediates, permutational isomers, could result. Those shown in Scheme 1 are illustrative of the point that either edge or facial attack towards the electron lone pair (topside attack) results in an intermediate which on β-scission yields phosphine oxide of retained configuration about phosphorus. The opposite stereochemical result arises from bottomside attack by *t*-BuO·. If pairwise permutational processes like those in (14) precede β-scission, then the stereochemical outcome from topside attack on the phosphine need not be retention. For example in Scheme 2, facial attack followed by a single permutation gives a permutational isomer which on β-scission yields product with inverted phosphorus configuration.

We have carried out just such a study using *t*-butyl hyponitrite as a thermal *t*-butoxy radical source.[28a] As indicated by equations (15)-(17), this reaction gives nearly stereospecific, retentive oxidation. The determination of stereochemistry of reaction (16) was made by comparison to the known stereochemically retentive process, equation (17). Thus, there is no evidence for formation of any intermediates from attack at any but the topside faces or edges of the phosphine (towards the lone pair). Further, no permutation processes prior to β-scission are required by the above result. One should qualify these conclusions by mentioning again the very recent evidence that a phenyl substituent on phosphorus may render the phosphoranyl radical tetrahedral rather than trigonal bipyramidal.[6] No proof concerning the configuration of the above intermediate is presently available.



Scheme 2. Effect of pairwise permutational isomerization on the stereochemistry of alkoxy-radical oxidation of a chiral phosphine.

$$t\text{-BuON=NOBu-}t \xrightarrow{65°} 2\,t\text{-BuO}\cdot + N_2 \qquad (15)$$

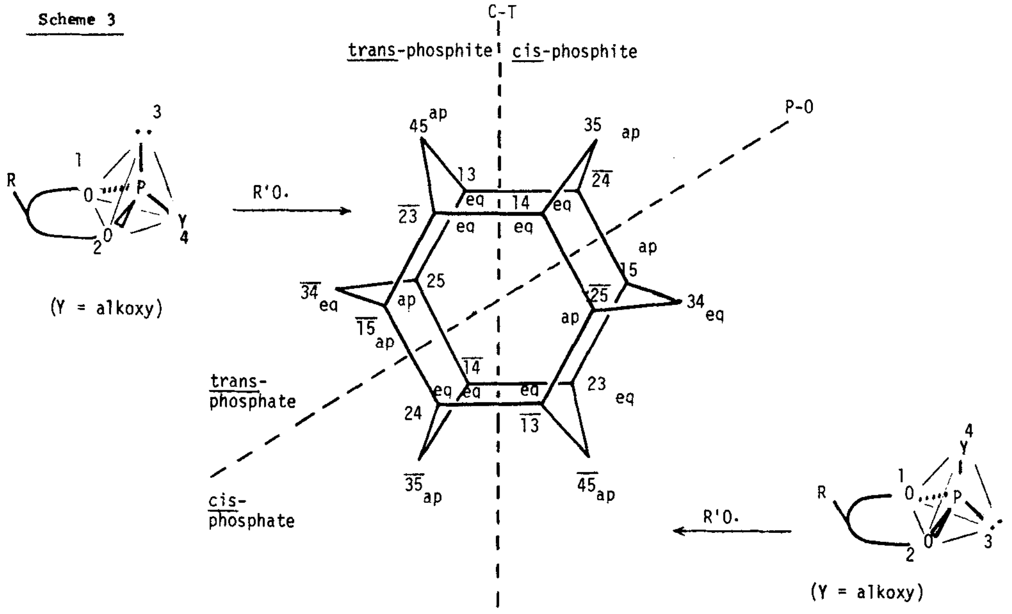


(16)

(17)

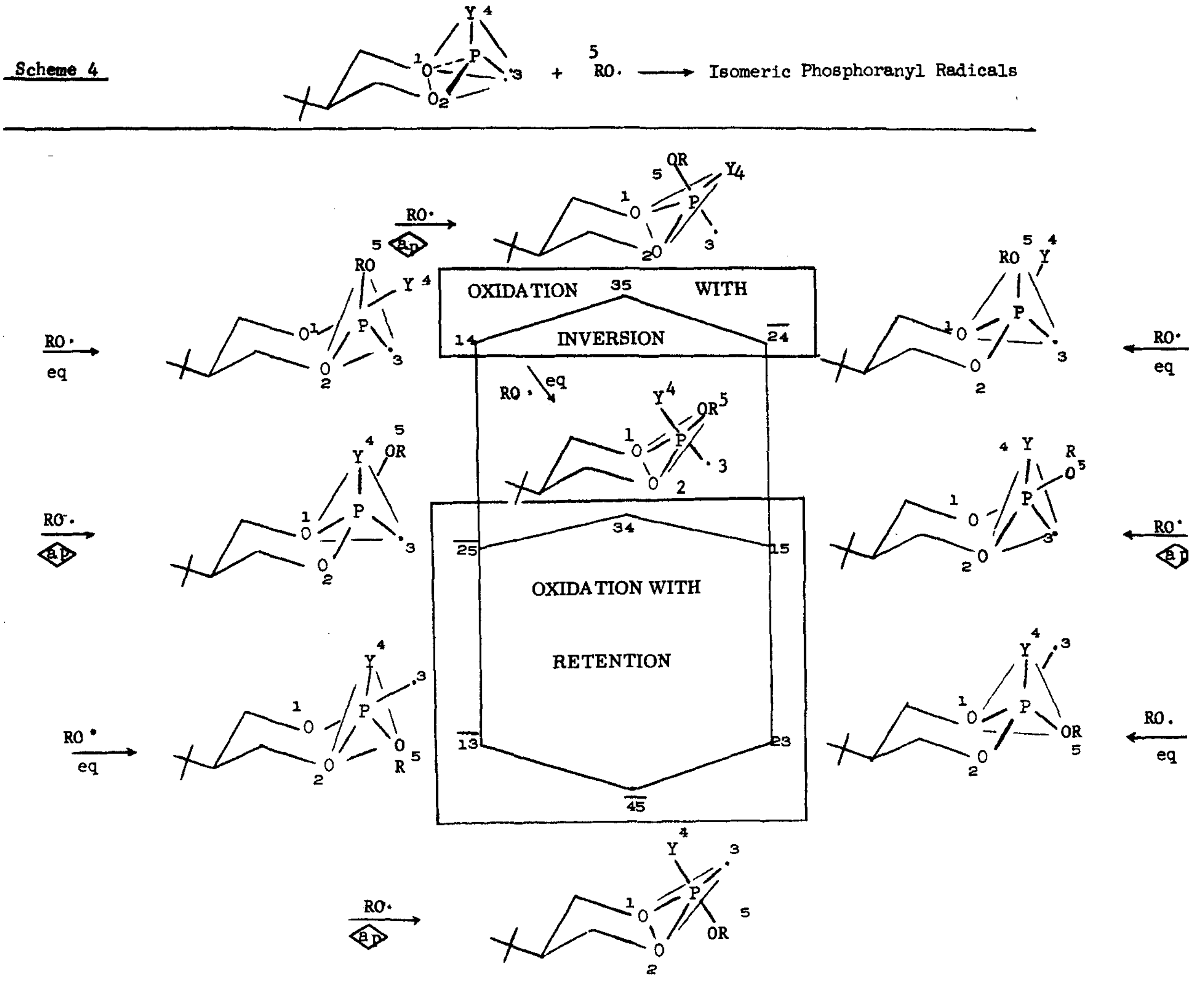
One could argue that the above system is biased against the sort of permutation which leads to inversion about phosphorus since in so doing a *t*-butoxy group is forced equatorial, and an alkyl or phenyl substituent must go apical – both in violation of presumed stereoelectronic preferences. To overcome this objection, we have examined the *t*-butoxy radical oxidations of certain cyclic phosphites (equation 18). Scheme 3 shows for *cis*/*trans* isomeric cyclic phosphites effects of direction of attack of the entering alkoxy group top or bottom and possible pairwise permutational isomerizations (mode 1[26a]) on the stereochemical outcome of oxidation. This diagram is the same as those Mislow and coworkers[27a] have applied to pentacovalent phosphorus systems. The number of a given permutational isomer indicates which substituents are apical. Isomers 12 and $\overline{12}$ are excluded since the ring oxygens cannot become co-apical. The difference between isomers labeled $\overline{45}$ and 45 is simply that $\overline{45}$ is derived from the *cis* phosphite and 45 from the *trans* phosphite. The designation ap or eq beside the number tells the position of the *t*-BuO group in that permutational isomer. Those phosphoranyl radicals to the right of the *c-t* (*cis-trans*) plane result from attack on the *cis* phosphite and *vice versa* for those to the left. the *p-o* plane separates *cis* and *trans* phosphates (oxides) formed on β-scission of the *t*-BuO C–O bond of the given permutational isomer. What is immediately evident is that a single permutation, e.g. 15 → $\overline{24}$, $\overline{25}$ → 14, $\overline{15}$ → 24, or 25 → $\overline{14}$, could result in product oxide with stereochemistry inverted at phosphorus.

Scheme 3



Scheme 3. Effects of mode of attack and pairwise permutational isomerization (mode 1) on the stereochemistry alkoxy-radical oxidation of stereoisomeric phosphites.

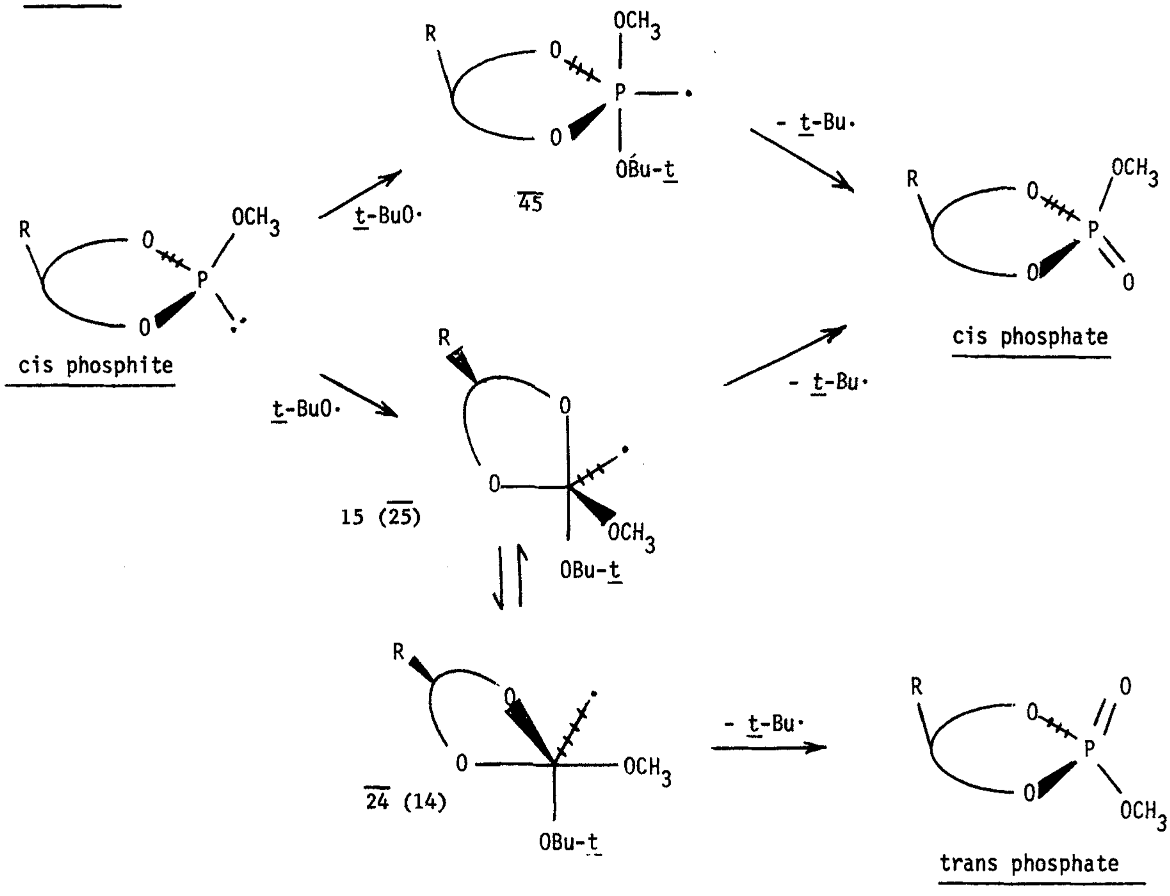
Half of Scheme 3 is given with structural detail in Scheme 4. Structures are shown for the permutational isomers formed on reaction of *t*-BuO with *cis*-2-methoxy-5-*t*-butyl-1,3,2-dioxaphosphorinane. The stereochemical outcome of β-scission from a given isomer is indicated. This scheme may be further simplified by assuming that 14, 35 and $\overline{24}$ are not formed *initially*. These correspond to the bottom side attack referred to earlier in the phosphine case and on β-scission give inverted product. (The lack of inversion in the phosphine suggests that 14, 35 and $\overline{24}$ do not form or are quickly isomerized.) Attack to give 14, 35, and $\overline{24}$ also should be sterically unfavorable. In systems in which pentacovalent phosphorus intermediates are formed, the assumption that the entering phosphorus ligand occupies an apical position has been found to be most useful in explaining stereochemical results.[25,27] If this postulate is applied to Scheme 4, one need then only consider the *initial* formation of intermediates 15, $\overline{25}$, and $\overline{45}$. In fact 15 and $\overline{25}$ are simply enantiomers, both of which yield product of the same stereochemistry.



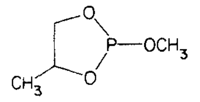
Scheme 4. Stereochemical considerations on oxidation of cis-2-methoxy-5-t-butyl-1,3,2-dioxaphosphorinane.

Scheme 5 is then the very much simplified permutational scheme with respect to which our studies of oxidations of both 6- and 5-membered ring phosphites may be discussed. Table III lists results of oxidation of phosphites **10** and **11** by *t*-butoxy radicals. More than one initial *cis*/*trans* ratio of starting phosphites was used. The reactions are highly stereo-selective if not stereospecific. It might be argued that the 6-membered ring favors exclusive formation of $\overline{45}$ since there is a suggestion^{25b} that in pentacovalent phosphorus the diequatorial attachment of such a ring is favored. Intermediate $\overline{45}$ would be required to undergo at least two permutations to give inverted product and include presumably high energy intermediates along the way with the odd electron apical. By such arguments, however, the 5-membered ring phosphite should be expected to give predominantly 15 ($\overline{25}$). Merely random attack by *t*-butoxy on the three least hindered pyramidal faces yields 15 ($\overline{25}$) two-thirds of the time. Furthermore, existing esr evidence^{2d,f} requires that in phosphoranyl radicals of this type (12 (12) the ring cannot be diequatorial as in $\overline{45}$ but rather is either rigidly equatorial-apical or undergoes a rapid permutation like 15 ($\overline{25}$) ⇌ $\overline{24}$ (14). Therefore, the results of Table III require that the permutation 15 ($\overline{25}$) → $\overline{24}$ (14) be slow relative to β-scission of the apical *t*-butoxy group. An alternative possibility is that β-scission takes place

Scheme 5



Scheme 5. Effects of pairwise (mode 1) permutational isomerization on the stereochemistry of t-butoxy radical oxidation of stereoisomeric phosphites.



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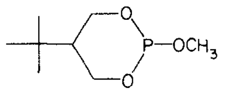

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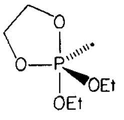


12

(18)

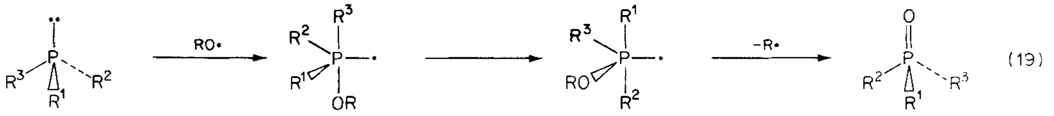
TABLE III (Ref. 28)
Stereochemistries of oxidations of 5- and 6-membered ring phosphites in benzene[a]

Phosphite	T° C phosphite[b]	*cis/trans* ratios Starting phosphite[b]	Product phosphate	% yield phosphates
10	17	46/54	45/55[c] (46/54)[b]	72
10	17	33/67	33/67[c] (33/67)[b]	71
11	65	90/10	95/5[c]	56
11	65	6/94	9/91[c]	43

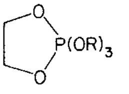
[a] [phosphite] = 0.3 to 0.5.
[b] By nmr.
[c] By glc.

only apical, regardless of whether $\overline{24}$ (14) is formed rapidly. Chemical labelling evidence which is discussed later, however, is best explained if both apical and equatorial β-scission occur.

These stereochemical findings are not consistent with a required isomerization prior to equatorial β-scission, as sometimes has been proposed[2b,d,i] to reasonably explain the relative stabilities of various alkyl-substituted phosphoranyl radicals (equation 19).



(19)



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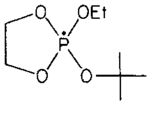
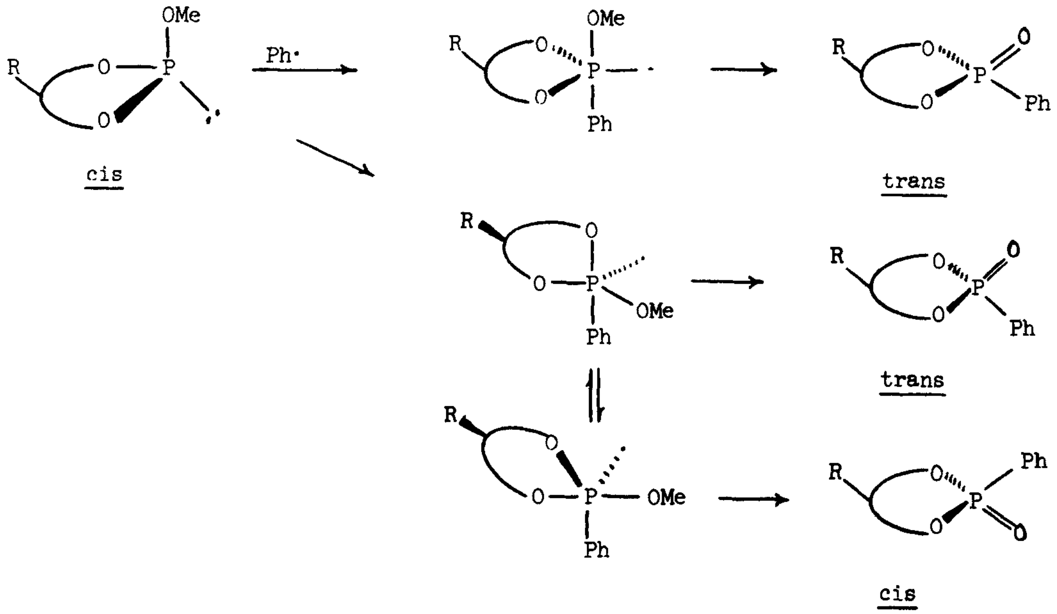


14

When compared to pentacovalent phosphorus systems such as **13**, the failure of 15 ($\overline{25}$) of Scheme 6 to undergo permutational isomerization in competition with β-scission is somewhat surprising. The rate of β-scission for **14**[2d] is about five times slower at –60° than that for t-BuO$\dot{P}$(OEt)$_3$. At the temperatures of our studies (17°) $\Delta G^{\ddagger}$ for t-butoxy β-scission of t-BuO$\dot{P}$(OEt)$_2$ is ~ 11 kcal/mol.[2b,d] Thus $\Delta G^{\ddagger}$ for the isomerization 15 ($\overline{25}$) → $\overline{24}$ (14) appears to be > 11 kcal/mol, since it is unable to compete with β-scission. It is quite certain that for **13** the permutation analogous to 15 ($\overline{25}$) → $\overline{24}$ (14) has $\Delta G^{\ddagger}$ several kilocalories per mole below 10 kcal/mol. Thus the phosphoranyl radical system has a surprisingly high permutation barrier when compared to the penta-alkoxy model.

Scheme 6

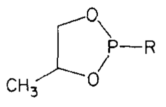


Scheme 6. Effect of pairwise permutational isomerization on the stereochemistry of a free-radical Arbuzov reaction of isomeric cyclic phosphites.

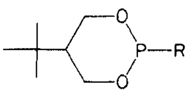
Another study of this type, which allows stereochemical information to be obtained, is the free-radical Arbuzov reaction of phenyl radicals with **10** and **11**. In Scheme 6 are depicted the phosphoranyl radical intermediates analogous to 45, 15 (25), and 24 (14) of Scheme 5. For such a reaction the propensity for the isomerization 15 (25) → 24 (14) to compete with β-scission should be greater than that in Scheme 5 since the phenyl and alkoxy move to positions favored by stereoelectronic considerations. However, the data of Table IV show that the stereochemical outcome of such reactions is that expected in the absence of permutational isomerization of 15 (25). The possible tetrahedral structures of the phenyl-substituted intermediates[6] again must be remembered.

A third sort of stereochemical study which we have carried out in cyclic trivalent phosphorus systems involves the substitution of an alkyl group on phosphorus by a dimethylamino radical (equation 20). The specific cyclic compounds studied were **15** and **16**. Radicals were generated by photolysis of the tetrazine $(Me_2N)_2N_2$.

$$Me_2N\cdot + R'P(OR)_2 \longrightarrow Me_2NP(OR)_2 + R'\cdot \qquad (20)$$



15 a, R = *t*-Bu
b, R = $PhCH_2$



16 a, R = *t*-Bu
b, R = $PhCH_2$

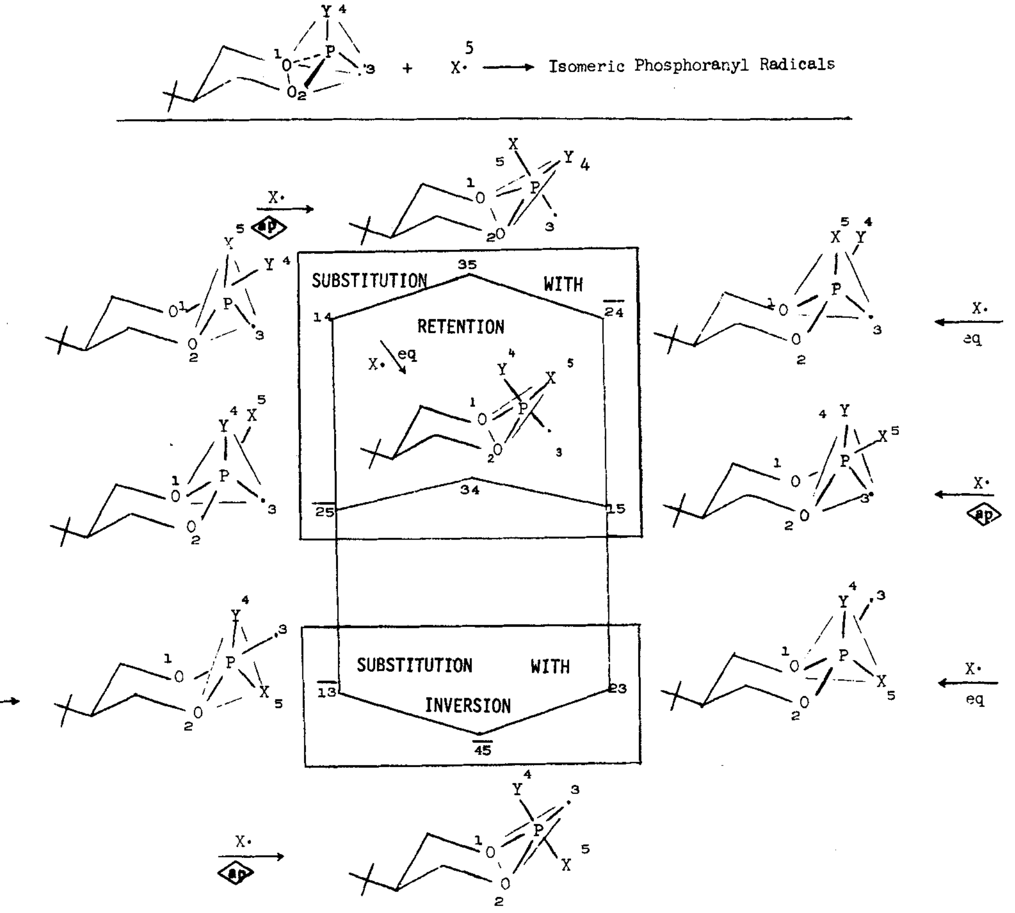
TABLE IV

Stereochemistries of free-radical Arbuzov reactions of phenyl radicals with cyclic phosphites in benzene at 22°[a] (Ref. 30).

Phosphite	*cis/trans* ratios[b] Starting phosphite	*cis/trans* ratios[b] Product phosphate	% yield phosphates
12	40/60	58/42	72
13	96/4	6/94	96
13	7/93	95/5	89

[a] [phosphite] ≅ 0.5.
[b] By pmr.

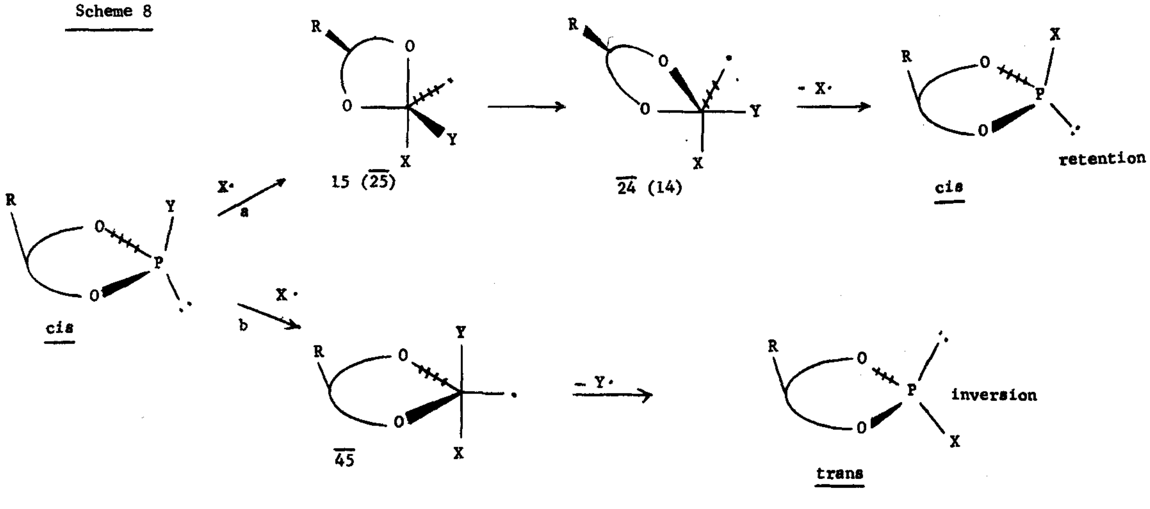
Scheme 7



Scheme 7. Effects of direction of attack and pairwise permutational isomerization on the stereochemistry of free radical displacement on isomeric 2-Y-5-t-butyl-1,3,2-dioxaphosphorinanes.

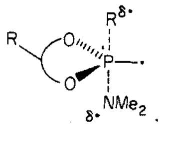
This sort of reaction is of special interest, not only since the stereochemistries of free radical substitutions are rarely determined, but also because *a priori* there appears to be a very good chance that retention of phosphorus configuration can occur. This is shown in Scheme 8 which is a simplification of Scheme 7 showing all possible initial radicals for the general case of displacement of Y by X·. (The simplification of Scheme 7 was done on the basis of the same assumptions used to obtain scheme 5.) Clearly, if both X and Y are equatorial or apical, inversion must occur. But should steric or electronic effects cause X and Y to be apical-equatorial (or *vice versa*), retention of configuration about phosphorus is predicted. Such a situation would be expected to be most likely in a 5-membered ring case if the strain rule of pentacovalent phosphorus systems applies.

Scheme 8



Scheme 8. Simplification of scheme 7.

Table V gives results[31] of the stereochemical investigations of the reactions of 15 and 16 with $Me_2N·$. (To our knowledge free-radical substitutions at heteroatoms have not been previously studied stereochemically.) In each case, inversion at phosphorus is the result, regardless of whether a 5- or 6-membered ring phosphonite is used. This perhaps surprising result could have one of several explanations. It is possible that substitution is in fact a concerted S_H2 process (structure **17**). Alternatively, it may be that these substitutions all proceed *via* intermediate $\overline{45}$, even though other intermediates are also formed. Phosphoranyl radical formation is probably reversible in this instance. Thus if isomerization of 15 ($\overline{25}$) to $\overline{24}$ (14) to place the leaving radical apical (as may be required so that X and Y both enter and leave apically) is slow, the formation of 15 ($\overline{25}$) may reverse, the entire reaction being diverted entirely through intermediate $\overline{45}$. The possibility that all of the reaction should proceed *via* $\overline{45}$ is not predicted by the previously mentioned esr work.[2d,f] But esr studies may indicate only the thermodynamic stability of an intermediate rather than whether its formation is kinetically favored. No evidence for the process 15 ($\overline{25}$) → $\overline{24}$ (14) is found.



17

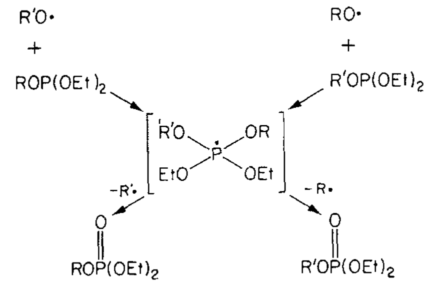
We have considered this system only in the context of a pairwise permutation process. It could be that some other permutation mode[26] permits 15 ($\overline{25}$) to be isomerized to an intermediate with Y(R) apical which then gives inverted product. We hope to examine other displacement reactions having groups of different electronegatives (e.g. R and RO) in which intermediate formation should be irreversible.

Another way to understand the modes of phosphoranyl radical formation and subsequent reaction is to use chemical labelling. In this approach one tries to generate the same intermediate in two or more ways (reaction 21) to see whether configurational effects influence the ratios of phosphates formed.

TABLE V
Stereochemistries of free-radical substitutions in benzene at 25° (Ref. 31)

Phosphonite	Initial[c] *cis/trans*	Reacted[b,c] *cis/trans*[b]	Product[b,c] *trans/cis*	Accountability[c]
16a	65/35	78/22	77/22	99
16a	48/52	73/27	72/28	92
16a	36/64	59/41	60/40	92
16a	87/13	79/21	80/20	94
16a	62/38	46/54	48/52	95
15a	32/68	36/64	30/70	90
15a	34/66[d]	38/62[d]	35/65[d]	–
15a	36/64	37/63	35/65	89

[a] $Me_2N\cdot$ from photolysis of $Me_2NN{=}NNMe_2$ at 25°.
[b] At 30% consumption of starting material, $[\text{phosphonite}]_0 \sim 0.3M$.
[c] By pmr unless otherwise noted.
[d] By vpc.



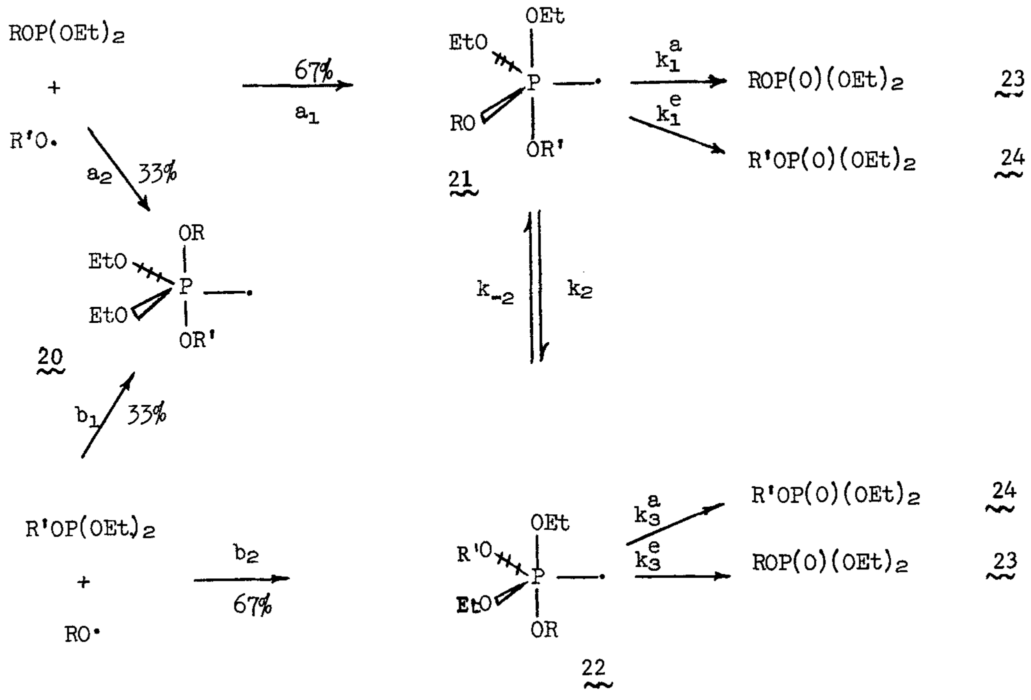
(21)

We earlier reported[32] a study of the reactions (22 and 23) of benzyloxy radicals with trialkyl phosphites. As shown, reactions (22) (15 replications) and (23) (10 replications) gave different ratios of phosphates **18** (p-$CH_3C_6H_4CH_2OP(O)(OEt)_2$) and **19** ($C_6H_5CH_2OP(O)(OEt)_2$. The memory effect displayed rules out: (1) a configuration (e.g. tetrahedral) for the phosphoranyl radical intermediate in which both benzyloxys are configurationally equivalent; (2) a configurationally random introduction of benzyloxys into apical and equatorial positions of a trigonal bipyramidal intermediate; (3) a permutational isomerization (e.g. **21** ⇌ **22**, Scheme 9) such that the benzyloxys are interchanged at a rate much faster than β-scission. These results were explained[32] in terms of a model based on the general Scheme 9. In Scheme 9 the attacking RO· or R′O· enters **20-22** stereospecifically in the apical position. Attack on the three least-hindered pyramidal phosphite faces (consistent with the above stereochemical work) is assumed to be random and therefore to give 33/67 initial ratio of **20/21** or **20/22**. Note that the ratio of phosphates **18/19** (corresponding to **23/24** in Scheme 9) from reaction (22) is very close to being within the experimental limits of error equal to the inverse ratio, **19/18**, in reaction (23). That is, **18/19** ≅ 1.20 in reaction (22) and **19/18** ≅ 1.20 in reaction (23). It was assumed[31] that $k_1 \gg k_2$ and $k_3 \gg k_2$, i.e. that the rate of β-scission was much greater than that for the pairwise permutational isomerism depicted by **21** ⇌ **22**. The ratios **18/19** and **19/18** of 1.20 are calculated from Scheme 9 assuming $k_1^a = k_3^a = k^a{}_\beta, k_3^e = k_1^e = k^e{}_\beta$ (β-scission rate essentially unaffected by methyl substitution), and the ratio $k^a{}_\beta / k^e{}_\beta = 1.3$. β-scission by this model ($k^a{}_\beta, k^e{}_\beta \gg k_2, k_{-2}$) is seen to be faster axial than equatorial ($k^a{}_\beta > k^e{}_\beta$). (The failure of the **18/19** ratios to be precisely inverse values in reactions (22) and (23) may be the result of a small effect of the p-methyl substituent.)

$$C_6H_5CH_2O\cdot + p\text{-}CH_3C_6H_4OP(OEt)_2 \longrightarrow \mathbf{18} + \mathbf{19} \tag{22}$$
(ratio **18**/**19**) = 1.15 ± 0.02

$$p\text{-}CH_3C_6C_4CH_2O\cdot + C_6H_5CH_2OP(OEt)_2 \longrightarrow \mathbf{18} + \mathbf{19} \tag{23}$$
(ratio **19**/**18**) = 1.25 ± 0.03)

Scheme 9



Scheme 9. Oxidations of trialkyl phosphites via configurationally stable phosphoranyl radical intermediates.

An important alternative model based on Scheme 9 which must also be considered[10] is one in which permutational isomerizations, **21** → **22** and **22** → **21** occur at rates comparable to and competitive with axial β-scission (i.e. k_1, $k_3 \cong k_2$, k_{-2} ; and $k^a{}_\beta \gg k^e{}_\beta$). (Since *via* path a or b of Scheme 9 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.) A steady state kinetic analysis for path a based on the concentration of **21** gives (24). (An identical treatment based on **22** can be done for path b.)

$$d[23]/d[24] = k_1^a(k_{-2} + k_3^a)\,dt/k_2k_3^a\,dt \tag{24}$$

If, as we have assumed, β-scission is essentially unaffected by the methyl label, then again $k_1^a = k_3^a = k^a{}_\beta$, where $k^a{}_\beta$ is just the rate of β-scission from the apical position. It is also reasonable that $k_2 = k_{-2}$. With these substitutions and integration, (24) gives (25). If 67% of reaction (22) (which gives **18**/**19** = **23**/**24** = 1.2) proceeds *via* path a, then the ratio **18**/**19** (**23**/**24**) formed *via* intermediate **21** is 1.3.

$$23/24 = (k_{-2} + k_3^a)/k_2 = 1 + \frac{k^a{}_\beta}{k_2} \tag{25}$$

From (25) it then follows that $k_2 = k_{-2} = 3.3k_1^a = 3.3k_3^a = 3.3k^a{}_\beta$. Thus the above results are readily explained if the permutational isomerizations **21** → **22** and **22** → **21** are about three times as rapid as β-scission from the apical position.

A choice between these two treatments can be made by lengthening the lifetimes of intermediates **21** and **22**.[10] Evidence from other studies (Table I) shows that β-scission involving cleavage of oxygen bonded to secondary carbon proceeds with a rate constant more than 300 times slower than that in which benzyloxy C—O scission occurs. In such a case, k_2 for R′O· or RO· in Scheme 9 should be at least 900 times k_1^a or k_3^a. Under such conditions complete equilibration of **21** and **22** prior to β-scission will occur. The ratio **23/24** then must be the same *via* either path a or b.

We generated the intermediates $s\text{-BuO}\dot{\text{P}}(\text{OEt})_3$ and $s\text{-PentO}\dot{\text{P}}(\text{OEt})_3$ at 65°, each by two independent routes (reactions 1 and 2 of Table VI). The corresponding phosphates were obtained in high yields, and the product ratios (**23/24**) are shown clearly to be *dependent* upon the direction of approach to intermediates **20, 21** and **22**. Similarly, the approach to intermediate $sec\text{-BuO}(sec\text{-PentO})\dot{\text{P}}(\text{OEt})_2$ *via* reactions (5) and (6) of Table VI failed to show product convergence. In reaction (7) the same phosphoranyl radical is generated by a third pathway. Thus, the second model based on Scheme 9 for the benzyloxy system is invalidated. We conclude that a permutational isomerization of the type shown in Scheme 9 for **21** ⇌ **22** is not competitive with β-scission involving benzyloxy groups. Whether **21** ⇌ **22** has become comparable in rate to β-scissions of primary and secondary alkoxy groups cannot be ascertained. What can be concluded is that in the studies of Table VI 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 a view[2b,d,i] that β-scission happens more rapidly from the equatorial position. To the extent that Scheme 9 is valid, we conclude that at the temperature studied $k^a_\beta > k^e_\beta$.

The sort of exchange shown by **21** ⇌ **22** is no more than competitive with β-scission (Table VI) of *sec*-alkoxy groups ($\Delta G^\ddagger \cong 12$ kcal/mol).[2d,10] As stated earlier, it is quite certain that $\Delta G^\ddagger$ for permutational isomerization of $(\text{RO})_5\text{P}$ is several kcal/mol less than 10 kcal/mol.[29] If a direct analogy is drawn between tetralkoxy phosphoranyl radicals and the pentacovalent system, then it is surprising that permutational isomerizations cannot compete with β-scission even when the latter processes involve a benzyloxy group. *The view that $(RO)_4P\cdot$ is simply an analog of $(RO)_5P$ seems to be an over simplification.*

Because of the possibility that the failure to observe identical ratios of products from two pathways could be some artifact of the system, a number of controls have been run. Reactions have been interrupted to check for alkoxy exchange in starting materials. Product phosphate was added at the beginning of reactions to test product equilibration. Different batches and concentrations of hyponitrites were used to test for oxidative impurities. The rate of diethyl hyponitrite decomposition was found to be unaffected by added phosphite. Reactions (1) and (2) of Table VI were carried out with $(sec\text{-BuO})_2$ and $(\text{EtO})_2$ as sources of alkoxy radicals using ultraviolet light at 16° without significant change in product ratios.

We are able to explain the oxidation of the seven phosphite oxidations of Table VI plus two others on the basis of Scheme 10 and the following assumptions:

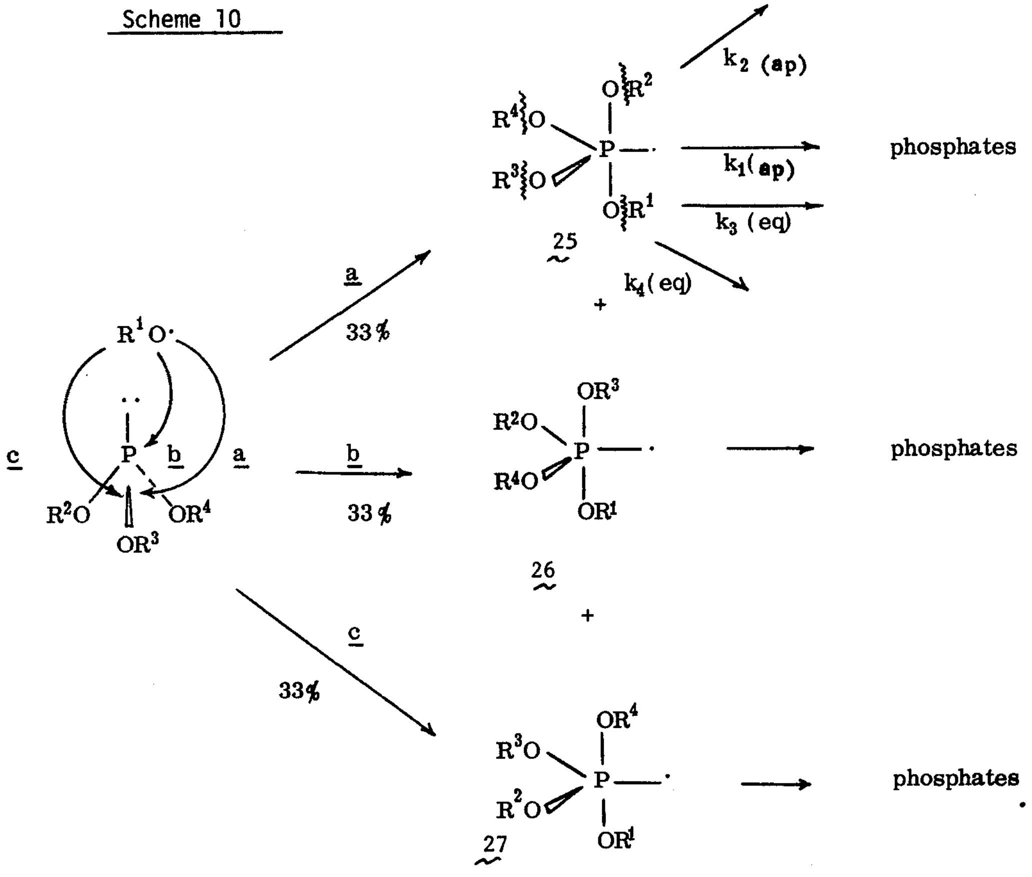
1) R′O is introduced apically into **25, 26** and **27**;
2) Random R′O·attack gives equal amounts of **25-27**;
3) β-scission occurs at both apical and equatorial positions;
4) The relative k_β values for various RO in equatorial or apical positions are:
    EtO (eq) = 1.0
    EtO (ap) = 2.1
    sec-BuO (eq) = 3.4
    sec-BuO (ap) = 4.5
    sec-Pent (eq) = 4.4
    sec-Pent (ap) = 4.9

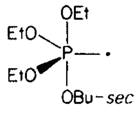
On this basis it is possible to predict the experimental values for all nine reactions with an average error of 6%. For example, reaction (26) will give intermediate **30** only whereas reaction (27) would lead to **32** formation two-thirds of the time.

$$sec\text{-BuO}\cdot + \text{P(OEt)}_3 \longrightarrow (\text{EtO})_3\text{PO}\ \mathbf{28} + sec\text{-BuOP(O)(OEt)}_2\ \mathbf{29} \qquad (26)$$

$$sec\text{-BuOP(OEt)}_2 + \text{EtO}\cdot \longrightarrow 28 + 29 \tag{27}$$

Scheme 10





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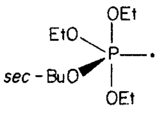

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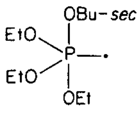

32

For reaction (26) the calculated 28/29 ratio is given by (28).

$$\frac{28}{29} = \frac{4.5}{(1)(2.1)+(2)(1.0)} = 1.09 \tag{28}$$

For reaction (27) the ratio is given by (29). The experimental values of Table VI are 1.07 and 0.75. The internal consistency of these results is gratifying in that the relative ease of β-scission follows radical stability, and there is at least a slight preference for apical β-scission in each instance.

Earlier we reported[14] that the reaction of ^{14}C-labelled *t*-BuO· with $(t\text{-BuO})_3\text{P}$ displayed no memory effect, the β-scissions of the four *t*-butoxy groups being random. If in $(t\text{-BuO})_4\text{P}\cdot$ $k^{a}_{\beta}/k^{e}_{\beta}$ were 1.3, the memory effect would not have been detectable within the error limits of the experiment.

TABLE VI (Ref. 10)
Products of β-scissions involving primary and secondary alkoxy radicals[a]

Reaction	Reactants				Products[b]		% yield[c]
	$R'O\cdot$	$RO\cdot$	$ROP(OEt)_2$	$R'OP(OEt)_2$	$ROP(O)(OEt)_2$ / $R'OP(O)(OEt)_2$	$ROP(O)(OEt)_2$ / $R'O(RO)P(O)OEt$	
1	*sec*-BuO·		$(EtO)_3P$		1.07 ± 0.03 (8)[d]		83-90
2		EtO·		*sec*-BuOP$(OEt)_2$	0.75 ± 0.04 (8)		88-93
3	*sec*-PentO·		$(EtO)_3P$		1.27 ± 0.01 (2)		96,96
4		EtO·		*sec*-PentOP$(OEt)_2$	0.95 ± 0.01 (2)		95,97
5	*sec*-BuO·	*sec*-PentO·	*sec*-PentOP$(OEt)_2$		1.03 ± 0.03 (4)	1.62 ± 0.03 (4)	93-95
6				*sec*-BuOP$(OEt)_2$	0.74 ± 0.05 (4)	1.26 ± 0.10 (4)	89-94
7	EtO·		(*sec*-PentO)(*sec*-BuO)POEt		0.83 ± 0.02 (10)	1.32 ± 0.04 (10)	87-94

[a] Solutions to 0.6 to 1.2 *M* in phosphite and 0.4 to 0.6 *M* in initial hyponitrite, RON_2OR or $R'ON_2OR'$, in degassed benzene were heated at 65°:

[b] Replicate ratios obtained from glc plots of area ratio vs. molar ratio for two products. Average error given.

[c] Based on amount of starting phosphite consumed. Glc analysis, internal standard method, sensitivity corrected.

[d] Number of replications in parentheses.

CONCLUSIONS

We draw the following conclusions from the above stereochemical and chemical labelling work.

1) Attack on phosphorus is stereochemically non-random and directed towards the phosphorus lone-pair electrons.
2) No evidence for a pairwise permutation, equation (14), in competition with α- or β-scission is found in cyclic systems.
3) The attacking alkoxy group enters the trigonal bipyramid in such a way as to not occupy apical and equatorial positions randomly.
4) A pairwise exchange of apical and equatorial substituents does not compete with β-scission where the RO group undergoing such a cleavage isPhCH$_2$O in non-cyclic systems.
5) No permutation process which *randomizes* apical and equatorial alkoxy groups in competition with β-scission is available even when RO is a secondary one. A permutation process competitive with β-scission cannot be excluded for secondary RO. (Non-cyclic systems.)

It therefore appears that whereas phosphoranyl radicals resemble truly pentacovalent phosphorus species in being trigonal bipyramidal in configuration and showing similar thermodynamic substituent preferences for apical or equatorial positions, there are likely to be important differences between the two. A pairwise permutation of substituents, equation (14), does not occur in tetra-alkoxy phosphoranyl radicals as rapidly as in the pentacovalent compounds. In a paper at the Symposium, Penkovsky and Gorlov stated that calculated energy difference between the trigonal bipyramidal and square pyramidal (odd electron apical) calculated by CNDO/2 methods is 25 kcal/mol, considerably higher than the 5 kcal/mol calculated for the same process for F_5P. Professor R. Hoffmann has recently informed us[33] of his extended Huckel calculations on the radical anion PO_4^{-4} which indicate that the distortion from trigonal bipyramidal to square pyramidal requires an unusually great amount of energy. Apparently present theory in this area is in agreement with our experimental findings. Calculations of barriers to other permutational processes will be of interest.

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