

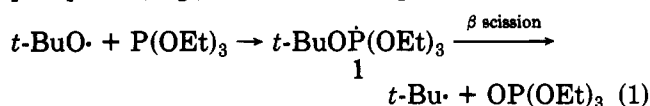
Phosphoranyl Radicals: Their Structure, Formation, and Reactions

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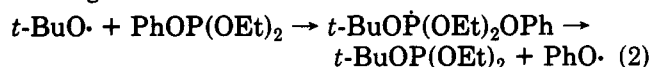
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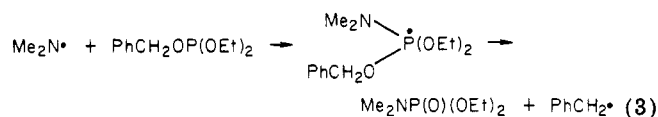
Since first suggested as a potential reaction intermediate in 1957,¹ the hypervalent free radical Z₄P• has been the subject of first chemical and later spectroscopic investigations. The designation phosphoranyl radical,¹ applied to Z₄P•, is an obvious reference to its potential homolytic derivation from phosphoranes, Z₅P. Among the earliest studied systems for which phosphoranyl radical intermediates were postulated are the reactions² of *t*-BuO• and RS• with phosphites and phosphines, e.g., reaction 1. Proposed intermediate 1,



formed by oxidative addition, undergoes β scission to give oxidation product, (EtO)₃PO. It was soon recognized³ that an alternate reaction, α scission, can occur, leading overall to substitution as in reaction 2.⁴



Thirdly, free-radical Arbuzov-like reactions take place when rapid β scission of a resident ligand follows addition of a radical to trivalent phosphorus, e.g., reaction 3.⁵ As an overall reaction, (3) is similar to the ionic



Arbuzov-type process: Me₂NCl + PhCH₂OP(OEt)₂ → Me₂NP(O)(OEt)₂ + PhCH₂Cl.

Our own fascination with phosphoranyl radicals as intermediates stemmed from simultaneous interests in free-radical chemistry and in the chemistry of truly pentacovalent phosphorus intermediates (Z₅P), which various Z₄P• resemble in a formal way if the odd electron is viewed as a pseudo fifth ligand. In recent years these radicals have caught the attention of free-radical chemists, among them ESR specialists,⁶ and also investigators working primarily in organic phosphorus chemistry. In addition, those interested in the structural and theoretical aspects of molecules and intermediates have become involved with considerations of geometries and electronic structures.

Our approach has involved largely chemical and stereochemical studies. In these we have attempted to understand the factors that determine the reactivity of

a given radical, Z•, toward PX₃ to form ZPX₃, as well as the structural features which influence the relative ease of the subsequent α and β scission steps. Further, we have tried to interrelate the above processes to the question of the overall reactivity of a given Z•/PX₃ system to yield a final, stable product. The question of whether ZPX₃ are indeed discrete intermediates has also received our attention. Knowledge of the geometries and electronic structures of phosphoranyl radicals and their susceptibility to permutational exchange (intramolecular ligand scrambling) of substituents on phosphorus has been vigorously pursued.

Structure

Phosphoranyl radicals were first detected as intermediates by ESR spectroscopy in the late 1960s. (See ref 6 and 7 for lengthy tabulations of spectra data.) Early work interpreted the large isotropic hyperfine phosphorus splittings encountered (600–1300 G) and nonequivalencies of otherwise identical ligands⁶⁻⁸ classically in terms of trigonal-bipyramidal (TBP) structures (local C_{2v}) such as 2 with the odd electron in an equatorial orbital approaching sp² hybridization. However, isotropic spectra of radicals with H apical^{9c,9}

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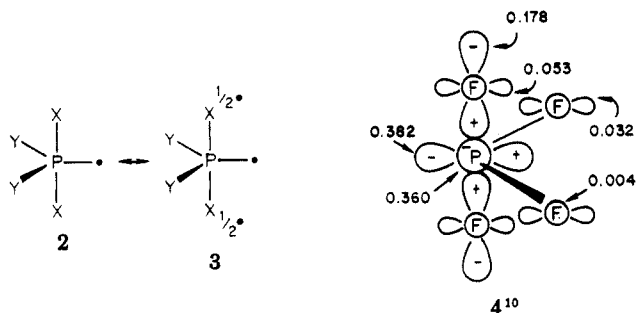
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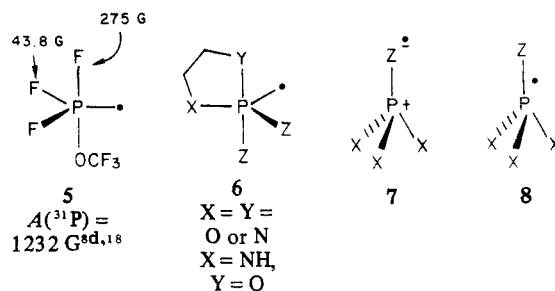
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Wesley G. Bentrude was born in Waterloo, IA, in 1935. He received his B.S. degree in Chemical Technology from Iowa State University and his Ph.D. in Organic Chemistry from the University of Illinois. Following his Ph.D. studies, he worked as a research chemist for the Celanese Corporation. After a postdoctoral year at the University of Pittsburgh, he joined the faculty at the University of Utah in 1964 and became Professor in 1972. His research interests include free-radical and organophosphorus chemistry.



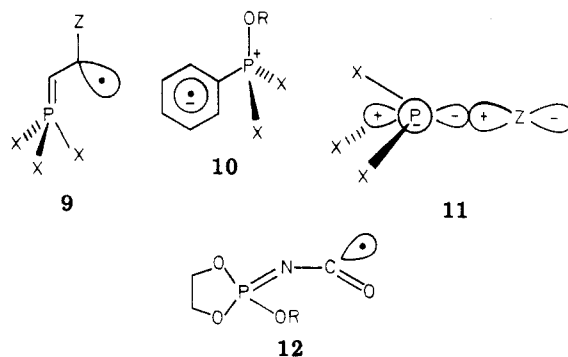
and anisotropic studies with substituents such as F¹⁰ and Cl¹¹ show a high proportion of spin density to be delocalized onto the apical substituents. This requires, in valence bond terms, contribution from an additional canonical form such as 3. This is a two-electron, three-centered apical bonding system with the odd electron in a nonbonding orbital. Hypervalent-bonding MO concepts place the odd electron in an orbital which possesses antibonding character and also distributes spin density onto both phosphorus and the apical substituents.¹⁰⁻¹² An example of such a proposed singly occupied molecular orbital (SOMO) is 4 (spin densities given).¹⁰ Structure 2 is still commonly used, however, since it accurately depicts geometry and is easily written.

Substituent apicophilicity (tendency of a group attached to phosphorus to be apical rather than the equatorial) orders determined by ESR include, for cyclic and noncyclic compounds, F, Cl, RCO₂ > RC(O)NR, OCN > RO, R₂N > H > R,^{8a} for cyclic compounds, *t*-BuO > EtO > C₄H₄N (pyrrolyl) > Me₃SiO;¹³ CF₃, (EtO)₂P(O)O > RO;¹⁴ for noncyclic compounds, Cl > CF₃ > RO;^{9b} Me₃Si(PhCH₂)N > RO;¹⁵ (RO)₂P(O)NMe > RO;¹⁵ CF₃O, (CF₃)₃CO, FCO₂, FSO₃ > F.^{8d} RO and R₂N are closer in apicophilicities in phosphoranyl radicals than in pentacovalent phosphorus compounds,¹⁶ though that of RO often is greater. Apicophilicities follow group electronegatives to a first approximation, but can be affected by the nature of the other substituents on phosphorus and by whether or not phosphorus is part of a ring.^{9b,13,17} An example that illustrates relative apicophilicities and the dependence of isotropic ligand hyperfine splittings on position (apical > equatorial) is 5. Whenever phosphorus is part of a



five-membered ring with either O or N bonded to phosphorus, the ring is attached apical-equatorial 6^{6e,j,7} as in truly pentacovalent systems.¹⁹ Oxygen is preferentially apical. Even the nitrogens in a six-membered ring are so attached. No quantitative assessment of these preferences has been made.

Though less common, phosphoranyl radical structures with non-trigonal-bipyramidal geometries and unusual odd electron distributions can be energetically favored (7-9). Structure 7 best represents certain likely tet-



rahedral species (π^* SOMO, ligand π radicals^{6i,j}) which have relatively low-lying π^* orbitals and display small (9-45 G) phosphorus hyperfine splittings.^{15,20} TBP and ligand π -phosphoranyl radicals are probably reasonably close in energies since configuration 10 is assumed when X is RO, but a TBP structure is populated when X cannot so readily support a positive charge on phosphorus (X = H, MeS, Cl, CF₃CH₂O).^{20c} Steric constraints can also be an influence.²¹ Radicals of the general type (CH₂=CHPX₂Y)• also are ligand π species,^{20a} as are tri- and tetraaryl radicals.^{6e,j,7}

Among radicals which possess local C_{3v} symmetry, have the odd electron in an antibonding σ_{PZ} orbital, and display reduced A_{iso}(³¹P) and increased hyperfine splitting constant to Z^{6i,7} (8) are (Ph₃PCl)²² and (X₃P-PX₃)⁺.^{6i,j,7} Strongly electronegative Z lower the σ^* MO energy, thereby stabilizing such radicals (e.g., SOMO 11²³). Likely a continuum of C_{2v} and C_{3v} structures exists.

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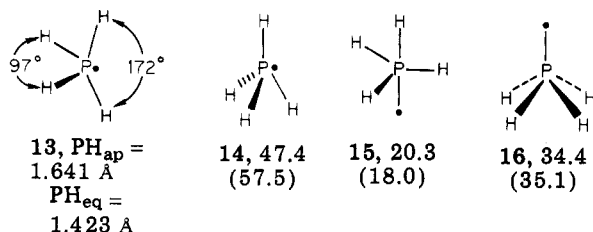
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One series of ligand σ radicals, **9**, has been reported.²³ These result from delocalization of spin density through ylide-like bonding (12). The existence of radicals too unstable for normal ESR detection has been inferred from several ³¹P CIDNP studies.²⁴ CIDNP is potentially a powerful tool for study of other Z₄P[•] systems of fleeting lifetimes.

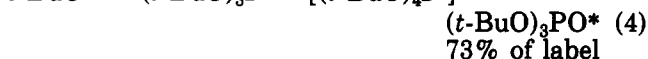
Theoretical calculations utilizing CNDO, INDO, Hückel, MS X α , and ab initio techniques^{8d,25} also assign TBP lowest energy structures to the majority of phosphoranyl radicals. Features include lengthened apical bonds and an angle involving phosphorus and the apical substituents somewhat collapsed from 180°. Structure **13** for H₄P^{•25g} is indicative (STO 4-31G ab initio level).



Calculated energies^{25g} for other geometries are given (kcal/mol) by 14–16. (Values in parentheses include d orbitals.) A similar energy variation for F₄P[•] was found.^{25g} Such calculations, of course, are better indicators of relative than of absolute energy differences. Interestingly, a sterically constrained, allegedly odd-electron-apical radical was recently reported (A_P = 686 G),²⁶ although this radical may in fact be a σ^* species.²⁷

Intermediacy

In spite of the hundreds of phosphoranyl radical systems observed,^{6a,7} it is not easy to ascertain whether a given radical characterized by ESR is indeed also the intermediate through which the major fraction of the reaction proceeds. Our chemical approach to this question gave one of the first positive answers. Thus, ¹⁴C-labeled *t*-BuO[•] reacts with (*t*-BuO)₃P (eq 4) to generate (*t*-BuO)₃PO containing 73% of the label as required for a near-random β scission of the four *tert*-butoxy substituents in [*t*-BuO]₄P[•].*²⁸ A number of



subsequent investigations, which will be discussed later in another context, gave similar results. Often, however, it is only assumed for convenience of interpretation that phosphoranyl radicals are in fact intermediates.

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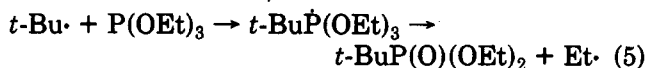
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Energetics and Rates of Formation

It became obvious following the very earliest investigations of the reactions of free radicals with trivalent phosphorus compounds that certain processes, though thermodynamically favorable overall, do not take place at all. Thus, the *tert*-butyl radicals resulting from β scission in reaction 1 do not react via free-radical Arbusov process 5,² even though it would be exothermic by more than 40 kcal/mol.²⁹



We have suggested that potential reactions of radicals Z[•] with PX₃ constitute three cases.^{6a,g,j,29} In case 1, addition takes place irreversibly and exothermally and with a near-diffusion-controlled rate. Flash photolysis, pulse radiolysis,³⁰ and competitive kinetic methods²⁹ have yielded second-order rate constants (k_p , M⁻¹ s⁻¹) for RO[•] reaction with Ph₃P, (EtO)₃P, Et₃P, and PhP(OMe)₂ in the range 8.1 × 10⁸ to 5.1 × 10⁹ at room temperature. Ph[•] reacts with (MeO)₃P similarly, k_p = 3.5 × 10⁸ (45 °C).^{31,32} An estimate^{33a} of k_p for reaction of RS[•] with (EtO)₃P (competitive rates) at 70 °C is 2.5 × 10⁸. Other likely case 1 radicals are Me₃SiO[•],¹³ BzO[•],^{6a} X₃P[•],³⁴ and (EtO)₂P(O)O[•].¹⁴ The exothermicity of phosphoranyl radical formation on addition of alkoxy radicals to trivalent phosphorus is estimated to be at least 20 kcal/mol.^{8b,29} Similarly, Ph[•] reaction is probably 10 to 15 kcal/mol exothermic.²⁹

Those reaction systems in which Z[•] adds to PX₃ reversibly comprise case 2. Net reaction requires a rapid subsequent α or β scission step to trap the intermediate phosphoranyl radical. Et[•],^{29,35} Me[•],³⁶ and Me₂N[•]^{29,35} give no net reaction with P(OEt)₃ even though clear evidence for the formation of MeP(OEt)₃ is furnished by ESR.³⁶ However, when PhCH₂OP(OEt)₂ is the reactant phosphite, these radicals are trapped by rapid β scission (reaction 3).^{29,35,36} Addition of Me[•] to (*i*-PrO)₃P, though reversible, is about 7 kcal/mol exothermic.^{8b} Reversibly formed phosphoranyl radicals also are trapped by rapid α scission, giving net substitution at phosphorus (eq 8).^{29,35} CF₃[•] and C₂F₅[•] are probably also case 2 radicals.^{9b} The major difference between cases 1 and 2 can be explained in terms of the relative strength of the PZ bond in the phosphoranyl radicals if one assumes that the bond strength order for such PZ bonds parallels that known for PZ₃.³⁷ (The average bond strength for (R₂N)₃P is uncertain.³⁸)

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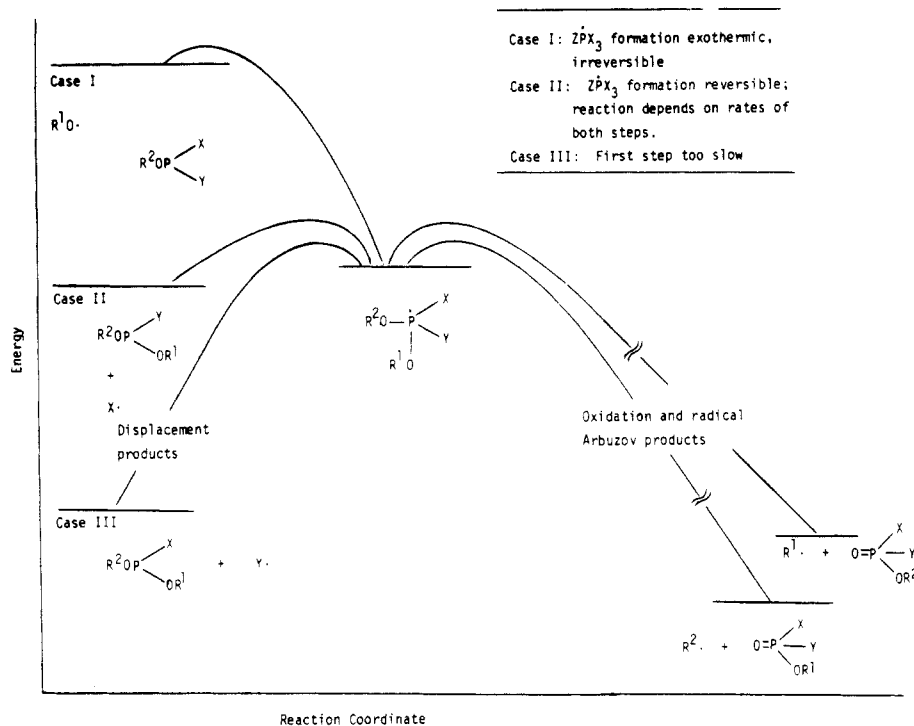


Figure 1. Effects of thermodynamics of phosphoranyl radical formation on overall reactivity.

Radicals which form very weak bonds to phosphorus will not add even reversibly. Such case 3 unreactivity is found for $PhCH_2\cdot$ and normally with *t*-Bu \cdot and *i*-Pr \cdot unless PX_3 is Ph substituted (see below).

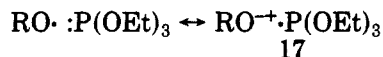
These ideas are brought together in the energy diagram of Figure 1. The position energetically of the products relative to $R^1O\cdot + R^2OPXY$ will simply depend on the energies of the bonds broken and formed. It is easy to see how bond strength considerations primarily control overall reactivity. $RO\cdot$ adds irreversibly,^{28,39} ultimately giving substitution or oxidation product. Progressive weakening of the PX or PY bonds in R^2OPXY results in increasing reversibility of the additions of $X\cdot$ and $Y\cdot$. An interesting comparison can be made between $Me_2N\cdot$ and $(Me_3Si)_2N\cdot$. The former adds so reversibly to PX_3 that such adducts have not been detected by ESR.¹⁷ The Me_3Si is bond strengthening, apparently, as phosphoranyl radicals from reaction of $(RO)_3P$ with $(Me_3Si)_2N\cdot$ are readily detected.⁴⁰

Representation of the intermediates $R^1OP(OR^2)XY$ as being isoenergetic is an oversimplification, especially when the geometry and electronic structure are changed by X and Y . Thus *i*-Pr \cdot and *t*-Bu \cdot both give radical Arbuzov reaction product with $ROPPH_2$ ⁴¹ but not with $(EtO)_3P$ or even $PhP(OEt)_2$,³⁵ and both $Me_2N\cdot$ and $Et\cdot$ induce the free-radical Arbuzov reaction of $PhP(OEt)_2$.³⁵ The phenyl-substituted phosphoranyl radicals are likely ligand- π species, perhaps of increased stability. Case 3 unreactivity probably can thereby be converted to case 2 reactivity.

Steric effects on reactivity have not been fully investigated. The equilibrium $Me\cdot + P(OR)_3 \rightleftharpoons MeP(OR)_3$, studied by ESR, responds to changes in the size of R .^{8b} Steric crowding has been proposed to account

for the instability of $(CF_3)_3\dot{P}OR$.^{8c}

Polar effects (structure 17) were suggested² early on



as contributing to the rapid reactions of $RO\cdot$ and $RS\cdot$. We were able to find, however, only very small uncorrelated effects of X on the reactivity *t*-BuO \cdot toward $XC_6H_4P(OMe)_2$ ($X = p\text{-H}, p\text{-MeO}, p\text{-Cl},$ and $m\text{-F}$).²⁹ The overriding factor in such rapid, near-diffusion-controlled reactions is the large PO bond energy. The somewhat less reactive *t*-BuOO \cdot oxidizes a series of PX_3 with relative rates correlated by σ^* with $\rho^* = -0.75$.⁴² The rates of autoxidations of Ph_2POMe , $PhP(OMe)_2$, and $(MeO)_3P$ decrease in the order listed, with $\rho^* = -0.38$.⁴³ Greater reactivity differences have been noted for *t*-BuO \cdot and $RS\cdot$ with various PX_3 ,^{33a} however, such a wide range of structural variation in PX_3 was involved that it is difficult to separate polar from steric effects. Large polar effects may yet be found in less reactive systems.

Stereochemistry of Formation

The stereochemistry of formation of ZPX_3 is an important consideration, especially when potential overall reaction stereochemistries are discussed. Whether Z enters the TBP intermediate initially in an apical or equatorial position is also of interest relative to the approximate microscopic reverse process, α scission. Though no direct, e.g., spectroscopic, experimental evidence is available, a reasonable working assumption is that on reaction with PX_3 (18) the attacking radical (Z) is introduced into ZPX_3 in the apical position to give 19, 20, or 21. Apical introduction of Z is supported by ab initio calculations of the reaction of $H\cdot$ with PH_3 ^{25g} (although the addition is thereby predicted to be en-

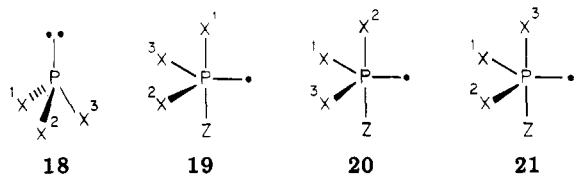
(39) W. G. Bentrude and T. B. Min, *J. Am. Chem. Soc.*, **98**, 2918 (1976).

(40) B. P. Roberts and J. N. Winter, *J. Chem. Soc. Chem. Commun.*, 545 (1978).

(41) R. S. Davidson, *Tetrahedron Lett.*, 3029 (1968).

(42) E. Furimsky and J. A. Howard, *J. Am. Chem. Soc.*, **95**, 369 (1973).

(43) Y. Ogata and M. Yamashita, *J. Chem. Soc., Perkin Trans. 2*, 730 (1972).



energetically unfavorable). The related radicals (RO)₃S[•] are formed by experimentally demonstrated apical introduction of RO[•] on attack at ROSOR sulfur.⁴⁴ Oxidative radical addition is the microscopic reverse of α scission. Apical bonds are expected to longer and presumably weaker (see structure 13) than equatorial ones, and kinetic evidence for preferential apical α scission is available.^{8b} (See later discussion.) A most interesting recent speculation⁴⁵ is that Z[•] is introduced initially (and lost in α scission) via the radical 8 having a P-Z σ^* SOMO. Isomerization then places Z specifically apical in the lower energy structures 19–21.

Furthermore, it is not known what factors, such as thermodynamic apicophilicity, may affect the initial positions of the various X substituents in 19–21 if all X are not the same. Evidence for random positioning of alkyl groups stems from studies of radical ratios following attack of *t*-BuO[•] on trialkylphosphines,^{8b} but this question has not really been addressed for non-identical X. If a transient σ^* radical is formed, then the first TBP radical resulting from it indeed could be the thermodynamically favored one. The opposite extreme would be random attack opposite X¹, X², X³ by Z[•] introduced directly apical. The rapid interconversions of isomeric phosphoranyl radicals, discussed later, makes the observation of possible initial adducts formed under kinetic control very difficult.

Permutational Isomerizations

A permutational isomerization may be defined in the context of a TBP geometry as a rearrangement, normally intramolecular in nature, which interchanges the positions of certain of the substituents over the TBP framework. Permutation mode refers to or specifies the particular type of rearrangement with respect to numbers and types of substituents (axial or equatorial) involved and the stereochemistry of the process without any regard to pathway (mechanism).⁴⁶ Initial questions regarding the permutational properties of phosphoranyl radicals were concerned with whether or not pairwise apical-equatorial exchanges with the odd electron as a sort of "electropositive" pivot group (a mode 1 permutation⁴⁶) might be rapid in analogy to pentavalent phosphorus systems. This later turned out not to be the case.

Our first approach to these questions involved the radioactive-labeling (memory effect⁴⁷) study, eq 4. The near-statistical cleavage affirmed the presence of the intermediate along the major reaction pathway and the equal reactivity of each of the four *tert*-butoxy groups toward β scission, a result later confirmed by ESR.⁴⁷ In subsequent work we generated potential common intermediates from two chemically independent pathways

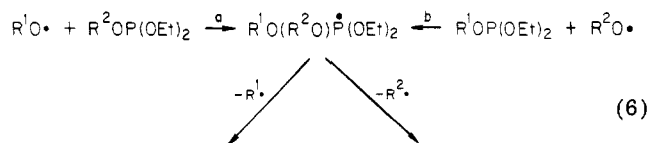
(44) J. W. Cooper and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 228 (1977).

(45) R. S. Hay and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 770 (1978).

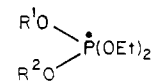
(46) Permutational modes are those codified (M₁–M₅) by Musher: J. I. Musher, *J. Am. Chem. Soc.*, 94, 5662 (1972); *J. Chem. Educ.*, 51, 94 (1974).

(47) D. Griller and K. U. Ingold, *J. Am. Chem. Soc.*, 97, 1813 (1975).

(a and b of eq 6). The ratios of the two phosphates



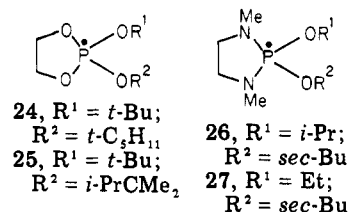
formed from alternative β scissions tell whether or not the intermediate is truly a common one. The observation of such a memory effect would require the reasonable assumptions of site selectivity of introduction of attacking alkoxy radical (discussed earlier) and a difference in apical and equatorial β scission rates. Neither radical 22,⁴⁸ for which we determined both alkyl



22, R¹ = *sec*-Bu; R² = Et

23, R¹ = Et; R² = *c*-C₄H₉

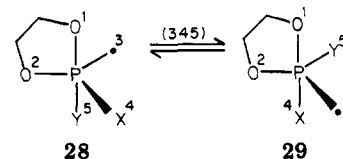
radical ratios (ESR) and product phosphate ratios, or 23,⁴⁵ investigated by the Roberts group using ESR, showed any memory effect, nor did the cyclic radicals 24 and 26 (alkyl radical⁴⁵ and stable product ratios⁴⁹), 25 (only ESR⁴⁵), or 27 (oxide ratios only⁴⁹). Origin-



independent product and radical ratios were also determined for the six-membered ring case analogous to 24.⁴⁹

Randomization of substituents in 22 and 23 is consistent with the rapid site exchanges observed by variable temperature ESR measurements on a variety of ROPX₃ (Z = H,^{9a} Me,^{8b} F¹⁸). At ~200 K, first-order rate constants of 10⁶–10⁷ s⁻¹ were noted. An *E*_a of 3.6 ± 1.0 kcal/mol was determined for *t*-BuOPMe₃, along with ΔG^\ddagger for *t*-BuOPH₃ and EtOPF₃ of 5.3 and 7.2 kcal/mol, respectively. Similarly, *E*_a for (C₄H₄N)P(OEt)₃ (C₄H₄N = 1-pyrrolyl) is 4.4 kcal/mol.¹³

ESR measurements on cyclic phosphoranyl radicals require interpretation in terms of the so-called mode 4 (exo) exchange^{8a,50} shown by 28 \rightleftharpoons 29 and conclusively exclude the mode 1 permutation possibility (*vide supra*). (The numbers in parentheses designate in ordered fashion the substituents undergoing permutation.) The

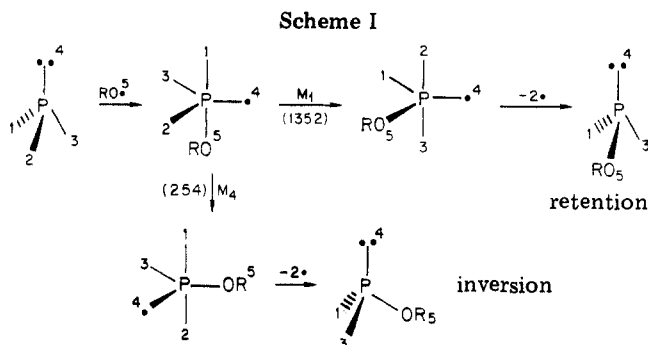


process occurs very rapidly with *k* = 10⁷–10⁹ s⁻¹ at ~200^{8a,14,17,45,50} and *E*_a values in the range 4–5 kcal/mol.^{17,45,50} The exchange 28 \rightleftharpoons 29 could easily account

(48) A. Nakanishi, K. Nishikida, and W. G. Bentrude, *J. Am. Chem. Soc.*, 100, 6403 (1978).

(49) A. Nakanishi, K. Nishikida, and W. G. Bentrude, *J. Am. Chem. Soc.*, 100, 6398 (1978).

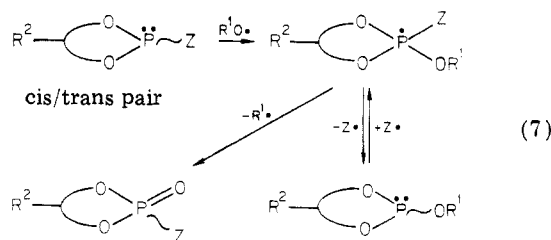
(50) B. P. Roberts and K. Singh, *J. Chem. Soc., Chem. Commun.*, 980 (1979).



for the lack of a memory effect in 24–27 since β scission has an E_a for *t*-BuO of 8–10 kcal/mol^{30b,c,45,51} (probably nearer 8 kcal/mol^{30b,45}) and for EtO of about 13 kcal/mol³⁶ and thus should occur more slowly than alkoxy exchange. ESR results have not allowed assignment of permutation mode in the acyclic cases. The randomization of R¹O and R²O in 22 and 23 may proceed via a process similar to 28 \rightleftharpoons 29. Placement of phosphorus ligands in a five-membered ring slows their exchange.^{8a,52}

Our second approach has been stereochemical. Scheme I indicates the potential effects of mode of ligand permutation on the overall stereochemistry of a free-radical substitution at a chiral phosphorus center. M₁ isomerization of the initial intermediate (formed via apical introduction of RO) followed by α scission results in retention. M₄ isomerization leads to inversion of configuration. In both isomerizations group 2 is placed apical prior to its departure via α scission, as implied by kinetic studies of α scission.^{8b}

Our initial study involved *tert*-butoxy radical oxidation of an optically active phosphine, which occurred with retention of configuration.^{53a,b} However, the intermediate in this case may be a permutationally stable tetrahedral ligand- π radical.²⁰ Subsequently, we examined free-radical oxidation, substitution, and Arbuzov reactions (eq 7) of five- and six-membered trivalent



phosphorus compounds (1,3,2-dioxaphospholanes and 1,3,2-dioxaphosphorinanes) of geometries known to us.⁵⁴ Specific systems investigated include the RO \cdot and RS \cdot oxidations of 34 and 38,^{53a,c} the substitution reactions of 30, 31, 35, and 36 with Me₂N \cdot ,⁵⁵ the substitution

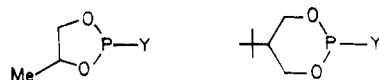
(51) G. B. Watts, D. Griller, and K. U. Ingold, *J. Am. Chem. Soc.*, **94**, 8784 (1972).

(52) D. Griller and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1416 (1973).

(53) (a) W. G. Bentrude, J. H. Hargis, N. A. Johnson, T. B. Min, P. E. Rusek, Jr., H. W. Tan, and R. A. Wielesek, *J. Am. Chem. Soc.*, **98**, 5348 (1976). (b) W. G. Bentrude, J. H. Hargis, and P. E. Rusek, Jr., *J. Chem. Soc., Chem. Commun.*, 296 (1969); (c) H. W. Tan and W. G. Bentrude, *J. Am. Chem. Soc.*, **96**, 5950 (1974).

(54) (a) W. G. Bentrude and H. W. Tan, *J. Am. Chem. Soc.*, **98**, 1850 (1976); (b) W. G. Bentrude and J. H. Hargis, *ibid.*, **92**, 7136 (1970); (c) W. G. Bentrude, H.-W. Tan, and K. C. Yee, *ibid.*, **97**, 573 (1975).

(55) W. G. Bentrude, W. A. Khan, M. Murakami, and H. W. Tan, *J. Am. Chem. Soc.*, **96**, 5566 (1974), and unpublished results.

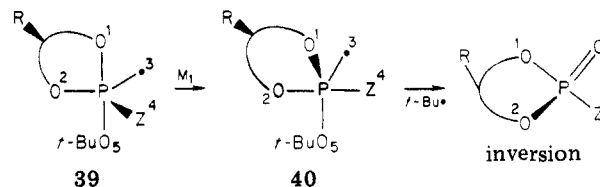


30, Y = *t*-Bu
31, Y = PhCH₂
32, Y = Et₂N
33, Y = PhCH₂O
34, Y = MeO

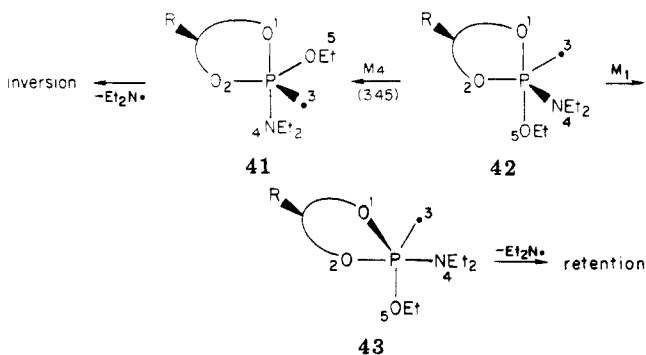
35, Y = *t*-Bu
36, Y = PhCH₂
37, Y = PhCH₂O
38, Y = MeO

reactions of 32 with EtO \cdot ,⁵⁶ and the free-radical Arbuzov reactions of 33 and 37 with Me₂N \cdot .^{5a}

The stereochemical analysis of such reactions in terms of the geometries of the initially formed phosphoranyl radicals, the potential ligand exchange processes available to them, and the consequent effects on overall reaction stereochemistry is necessarily very complex. Elsewhere^{53a} we have used the sort of M₁ topological graph that has proven useful in similar analyses of the pentavalent phosphorus reaction stereochemistry¹⁹ to sort out the permutational consequences of the experimentally observed near-stereospecific *t*-BuO \cdot oxidation of *cis/trans* mixtures of 34 and 38. We ruled out the occurrence of extensive amounts of M₁ permutation in competition with β scission. More specifically we argued that on reaction of the *cis* diastereomer, structure 39 should be formed in significant amounts, perhaps even initially, since (1) apical-equatorial geometry is statistically probable, (2) only radicals of such geometry have been observed by ESR where 5-membered rings are concerned, and (3) cogent arguments favoring apical introduction of attacking radical can be made. (See above.) In such a case the failure to observe inversion means that the interconversion 39 \rightarrow 40 must have ΔG^\ddagger greater than ΔG^\ddagger for β scission, 11 kcal/mol (from data of ref 45, 51).



Similarly, the free-radical Arbuzov and substitution reaction stereochemistries preclude extensive M₁ exchanges. Thus, isomerization of 42 to 43 prior to α scission gives product with retained phosphorus configuration, contrary to experiment.⁵⁶ Note, however, how a single M₄ process (42 \rightarrow 41) places the Et₂N apical prior to scission (microscopic reverse of attack) and gives inversion. Steps 39 \rightarrow 40 and 42 \rightarrow 43 em-



ploy the odd electron as electropositive pivot and are the exchanges expected to be most rapid if phospho-

(56) A. Nakanishi and W. G. Bentrude, *J. Am. Chem. Soc.*, **100**, 6271 (1978).

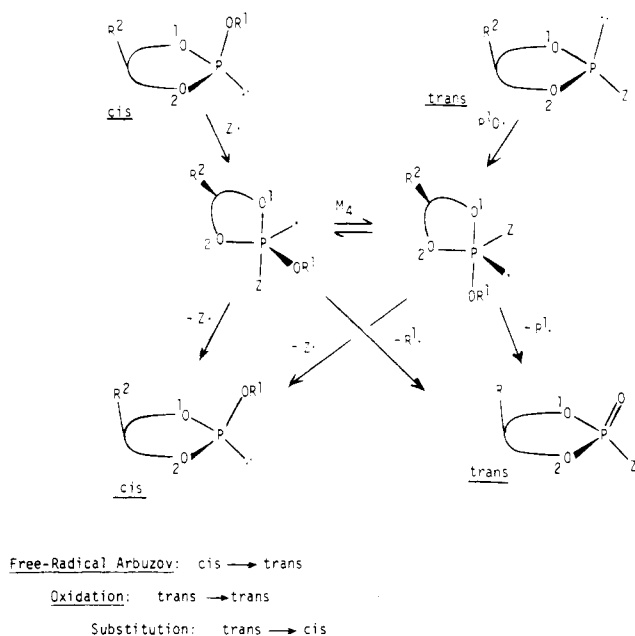


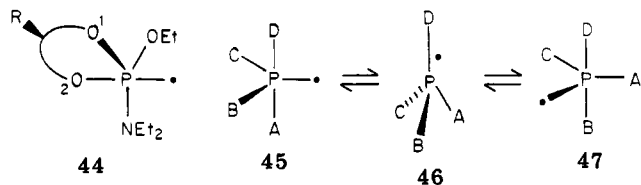
Figure 2. Correlation of observed stereochemistries of free-radical reactions of cyclic phosphorus compounds with potential M_4 permutations.

ranyl radicals were equivalent in permutational properties to truly pentacovalent phosphorus species.

The stereochemical results exclude M_2 and M_3 permutations of 39 and 42, but not the M_5 anti-Berry exchange,⁴⁶ which is ruled out, however, by ESR work.^{8a,50}

In Figure 2 the effects of M_4 (exo) exchanges on the stereochemistries of all three free-radical processes are correlated. Since the overall stereochemistries are unchanged by the M_4 (exo) processes, the observed stereochemical results do not require such a process to be operative but are highly consistent with the rapid M_4 (exo) exchanges observed by ESR.^{8a,50} Thus, the conclusion that phosphoranyl radicals are permutationally different from pentacovalent phosphorus analogues arises in complementary fashion from both stereochemical and ESR work.

A further clarification is needed in that observed permutational properties discussed are overall M_4 , and such exchanges could occur by successive permutations of other modes as is always possible for any mode other than M_1 .^{46,56,57} An example is the M_4 (exo) exchange, e.g., 42 \rightarrow 41, via two successive M_1 processes involving the "odd-electron-apical intermediate" 44. Regardless,



phosphoranyl radicals would still be permutationally dissimilar to pentacovalent phosphorus species in that such an overall M_1 phenomena must occur via "odd-electron-apical" intermediates of energy lower than the transition state for an M_1 process with odd electron as equatorial pivot.

Theory also is in accord with the above ideas concerning the permutational properties of phosphoranyl

radicals. Calculations at the ab initio^{25g} (vide supra) and CNDO^{25h,i} levels both place the energy of the square pyramidal radical 16 at higher energy than the "odd-electron-apical" structures such as 15. Radical 16 would be the barrier species for an odd-electron-pivot, M_1 process of a Berry pseudorotation type. Thus the same theory which coincides with experiment in predicting that fast M_1 isomerizations through square-pyramidal (SP) barrier states should be found for PF_5 ²⁵ⁱ says that $F_4P\cdot$ (or $H_4P\cdot$) should be more stable as a TBP, odd-electron-apical²⁵ⁱ or C_{3v} σ^* species (8)^{25h} than as SP 16.

Since CNDO calculations^{25h} place σ^* intermediates like 8 only 0.9–3.4 kcal/mol above the TBP species, an attractive low energy M_4 isomerization process^{45,50} is that via the sequence 45 \rightleftharpoons 46 \rightleftharpoons 47. It has been noted that the ligands A, B, and C undergo very little change in bonding in the process.^{25h} By contrast a considerable rehybridization energy must accompany transformation of 45 or 47 into the equivalent of 16. For 42 \rightarrow 41 the σ^* intermediate would have the odd electron in a P–O₁ antibonding orbital. Other low energy M_4 permutations are favored by ab initio methods.^{25g} One of these is essentially a (TR)² process.^{19e,f}

Whether a one-step M_4 process, a succession of M_1 isomerizations (or those of other modes) through odd-electron-apical intermediates, or permutations via intermediates analogous to 46 occur, phosphoranyl radicals are quite different in their permutational properties from what would be expected on the basis of the assumption that the odd electron is simply a sort of electropositive pseudoligand. Of course to assume that radicals and fully covalent, closed-shell species should necessarily undergo changes in geometry in strictly analogous fashion is unrealistic.

Figure 3 is one of two topological graphs that are required to show the effects of M_4 permutations of substituents, both exocyclic to the ring and endocyclic to it, on the stereochemistries of oxidation of cis and trans cyclic phosphite. As in similar diagrams,^{5a,19a,g,53a} the CT vertical plane separates initial adducts formed from attack of $R^1O\cdot$ on cis (left side) or trans phosphite (right side). The position of R^1O in each permutamer is designated by eq or ap. The numbers assigned to each isomer designate the pair of substituents which are apical. Unbarred numbers, e.g., 45, are those in which the equatorial substituents are encountered in a clockwise direction when viewed from the lower number, apical substituent. Permutamers 45, 25, 15, and 35 are the potential initial adducts from apical introduction of $R^1O\cdot$ as it attacks the cis phosphite. (Steric considerations probably exclude initial 35 formation.) The corresponding adducts for reaction of the trans phosphite appear only on the complementary diagram not shown. Since phosphorus configuration is retained on oxidation, 45, 25, and 15 do not undergo isomerization to the species above the P–O plane (the odd-electron-apical permutamers (34, 23, 13, 35)), or at least the latter do not undergo β scission. If indeed radicals 15, 25, and 45 undergo permutational exchange only via σ^* intermediates, then the intermediates above the P–O line are precluded from formation from 15, 25 and 45, and only cis phosphate can result.

Reactions

Unimolecular α and β scission processes are the most important product-forming steps available to phos-

(57) M. Gielen, "Applications of Graph Theory to Organometallic Chemistry", A. T. Balaban, Ed., Academic Press, New York, 1976, Chapter 9.

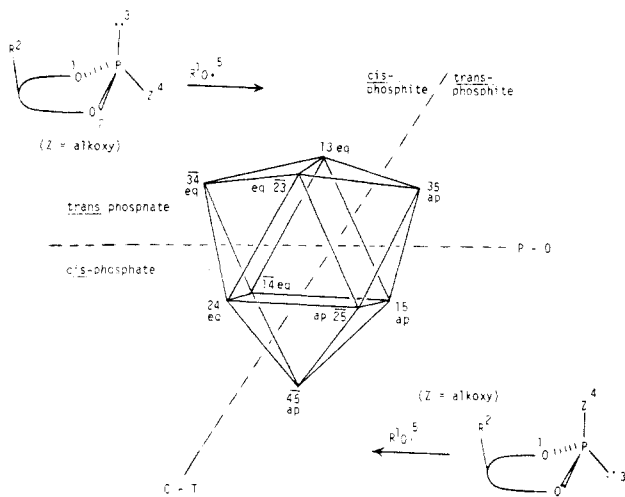
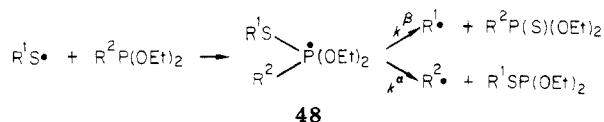


Figure 3. Effects of M_4 isomerization on the stereochemistry of $RO\cdot$ oxidation of cyclic phosphites.

phoranyl radicals. The competition between α and β scission is determined to the first approximation by the relative strengths (and changes therein) of the bonds undergoing cleavage. E.g., we determined^{4a,b} that for reaction of $t\text{-BuO}\cdot$ with a series of $ZP(OEt)_2$, nearly exclusive oxidation occurs for cases having average bond strengths of PZ_3 (D_{PZ} ³⁷) greater than 75–80 kcal/mol ($Z = RO, Ph$). For $Z = n\text{-Bu}_2N, PhO, Et, t\text{-Bu}$, and $PhCH_2$, substitution accounts for more than 95% of the product of $t\text{-BuO}\cdot$ reaction. $Z = Cl$, an intermediate case ($D_{PZ} = 77$ kcal/mol³⁶), gives products of both substitution and oxidation. Use of $PhCH_2O\cdot$ in place of $t\text{-BuO}\cdot$ results in more oxidation (presumed β scission), with the β/α ratio decreasing in the order $Z = PhO > n\text{-Bu}_2N > Me > Et > t\text{-Bu} > PhCH_2$.⁴ Interestingly, for the series $RO > PhO > R_2N > R$ a substitution order is found such that any group Y in the series can be displaced by any radical $Z\cdot$ to the left of it in the substitution process of eq 8.³⁵



From various ESR³⁶ and product studies,^{39,48,49} ease of β scission is seen to decrease in the order $PhCH_2O > CH_2=CHCH_2O > t\text{-BuO} > i\text{-PrO}, sec\text{-BuO}, c\text{-C}_6\text{H}_5 > EtO > MeO$. Reaction of $RS\cdot$ with the series of $ZP(OEt)_2$ gives almost entirely oxidation products,⁴ in keeping with the relative weakness of the RS bond. With certain alkylphosphonites both oxidation and substitution could be observed via the presumed intermediate 48. Changes in $E_a^\beta - E_a^\alpha$ and k^β/k^α were



noted for this reaction system on changing both $R^2\cdot$ and $R^1\cdot$ stabilities.⁵⁸

A large number of kinetic ESR investigations also have shown the effect of bond strengths on the scission processes of phosphoranyl radicals. E_a values for β scissions of various $t\text{-BuOP}(OR)_3$ to form $t\text{-Bu}\cdot$ are in the range 8–10 kcal/mol^{30b,c,45,51} (likely nearer 8 kcal/mol^{30b,45}) whereas that for $(EtO)_4P\cdot$ giving the ethyl radical is 13 kcal/mol.³⁶ Although a single phenyl

(58) W. G. Bentrude and P. E. Rogers, *J. Am. Chem. Soc.*, **98**, 1674 (1976).

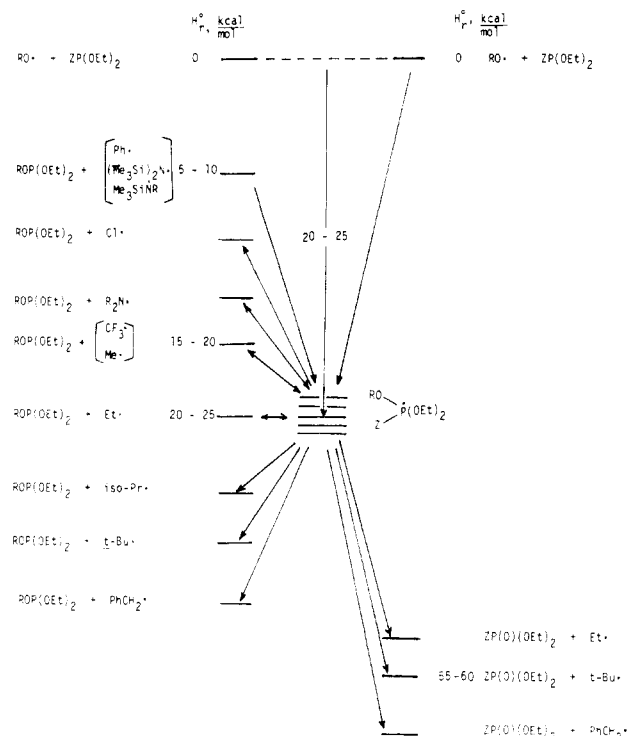


Figure 4. Estimated heats of reactions of various phosphoranyl radical processes.

substitution which makes the phosphoranyl radical a ligand- π species has no effect on the β scission of $[t\text{-BuOP}(OEt)_2Ph]\cdot$ ($E_a = 8.5\text{--}8.8$ kcal/mol),^{30b,59} $[t\text{-BuOPPh}_3]\cdot$ has an E_a of 12 kcal/mol.^{30a} Both α ¹⁷ and β ³⁶ scission are markedly slowed by inclusion of the bond undergoing scission in a five-membered ring containing the phosphorus atom and by the attachment of strongly electronegative substituents to phosphorus.^{8b,51} Expansion of the ring to six atoms speeds the rate of β scission relative to noncyclic radicals³⁶ and allows α scission to become rapid as well.¹⁷

In Figure 4 is summarized our current assessment of the approximate energetics of phosphoranyl radical formation and the overall change in enthalpy accompanying substitution, oxidation, or free-radical Arbuzov reaction. The double-headed arrows designate those cases in which the given radical has been demonstrated to be both a reactant and displacement product. The estimate of $\Delta H_r^0 = -7$ kcal/mol for $Me\cdot + (i\text{-PrO})_3P \rightarrow (i\text{-PrO})_3PMe$ ^{8b} (vide supra) and the average bond energies³⁷ for Me_3P and $(RO)_3P$ serve to fix the relative energy of the manifold of phosphoranyl radicals. The displacement of $Cl\cdot$ and $R_2N\cdot$ may be energetically less favored than shown. However, they can be displaced, whereas there is no evidence for displacement of the silylamino radicals⁴⁰ (which likely form stronger P-N bonds) or $Ph\cdot$.²⁹

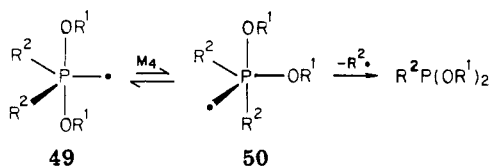
The question of apical vs. equatorial site selectivity for both scissions has been studied chemically and by ESR. Our own chemical labeling work⁶⁰ involving the intermediate radical $p\text{-MeC}_6\text{H}_4\text{CH}_2\text{OP}(OCH_2Ph)(OEt)_2$, formed from reaction of the benzyloxy and p -methylbenzyloxy radicals with the corresponding phosphites, was interpreted in terms of more rapid β

(59) Footnote in ref 20a.

(60) W. G. Bentrude and T. B. Min, *J. Am. Chem. Soc.*, **94**, 1025 (1972).

scission from the site of initial introduction of the attacking radical, presumably the apical position. Since there is now some question as to the ability of even benzyloxy groups to undergo β scission rapidly enough to compete with apical-equatorial ligand exchange,⁴⁵ it would be good to recheck this result by ESR or chemically with an independent source of benzyloxy radicals. Recent ESR results using cyclic phosphoranyl radicals appear to be consistent with preferential equatorial β scission,¹³ but the question is not yet settled.

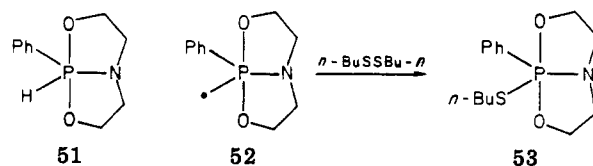
By contrast on the basis of kinetic work,^{8b,61} there seems to be little doubt that α scission is site selective, probably occurring more rapidly apical. The proposal^{8b} that the α scission of $R_2\dot{P}(OEt)_2$ requires a prior permutational isomerization (49 \rightarrow 50) means that the



stability of a phosphoranyl radical toward α scission depends both on the strength of the bond undergoing cleavage and the energetic ease with which the permutamer placing that bond apical can be populated. An interesting unifying concept is the idea of Roberts that σ^* -phosphoranyl radicals are the initial adducts of radical attack on trivalent phosphorus, the species by which the microscopic reverse, α scission, occurs from the apical site, and the intermediates through which permutational isomerizations take place.^{27,45,50}

Bimolecular reactions of phosphoranyl radicals include reactions with O₂,^{51,62} *t*-BuNO,⁶³ 5,5-dimethyl-1-pyrroline 1-oxide,⁶⁴ CCl₄,⁶⁵ alkenes,^{52,66} alkynes,⁶⁷ and alkyl radicals.^{51,68} We have recently shown that disulfides effect the alkylthiation of hydrido-phosphorane 51. The key step is likely 52 \rightarrow 53.⁶⁹ Bimolecular reactions are seen kinetically,⁷⁰ but reaction

products, e.g., P(V)-P(V) dimers, have not been isolated.



Concluding Remarks

Research on phosphoranyl radical systems has reached a somewhat mature stage. The electronic structures and geometries available have been defined. Overall reactivity in the oxidative addition of radicals to trivalent phosphorous can be understood in terms of bond strength factors and the rates of subsequent α and β scissions. The factors that control the latter are largely understood. The permutational properties of phosphoranyl radicals have been shown to be different from those of pentacoordinate species, and the importance of such isomerizations prior to α scission seems clear. Reactions involving the phosphoranyl radical as a discrete entity also have been described.

On the other hand, concrete experimental evidence for the stereochemistry of the introduction of a radical (*Z*-) attacking trivalent phosphorous (PX₃) is not available. This includes details as to whether *Z* is indeed initially apical, whether the initial adduct is in fact a σ^* species, and whether various X are initially in positions of greatest thermodynamic stability or more randomly disposed. The question of the extent to which phosphoranyl radicals lie on the major reaction pathway, especially when no intermediates are ESR detectable, is an important one. The stereochemical preference for β scission, apical or equatorial, is yet somewhat uncertain. The details of the permutation mechanism by which these radicals rearrange are perhaps beyond experimental determination, though still of interest. Although a general preference for apical/equatorial attachments of ring atoms to phosphorus is clear, no assessment of its magnitude by study of radicals with two strongly apical nonring substituents has been made. Bimolecular kinetics of radical decay at low temperatures are found, but the products have not been reported. The possibility of phosphorus-phosphorus coupling is an intriguing one. Finally, the preparative possibilities of phosphoranyl radical systems have not been fully explored.

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