

tigation. In any event, if monomeric mesitylmetaphosphonate, is formed both in pyrolysis and by decomposition of the Diels–Alder adducts, it polymerizes especially readily; if the polymerization is subject to any steric effect, that effect is quite insufficient to allow the easy isolation of the monomeric mesitylmetaphosphonate. Nevertheless the metaphosphonate presumably has been formed by the processes outlined in this paper.

Acknowledgments. The authors wish to thank Professor F. H. Westheimer for many helpful discussions during the course of this work. We also would like to acknowledge gratefully the support of the National Science Foundation through Grant CHE-77-05948 awarded to Professor Westheimer.

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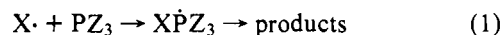
Free-Radical Reactions of Organophosphorus Compounds. 9.¹ The Question of Memory Effects in the Alkoxy-Radical Oxidations of Cyclic Trivalent Phosphorus Derivatives

Akira Nakanishi, Koichi Nishikida, and Wesley G. Bentrude*

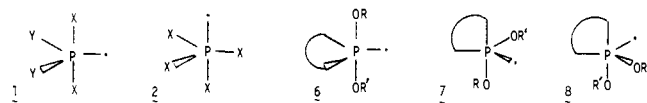
Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. Received February 2, 1978

Abstract: Alkoxy-radical oxidations of a series of five- and six-membered ring phosphites and several five-membered ring phosphorodiamidites (1,3,2-diazaphospholanes) were studied. Determinations of product oxide ratios were made in reaction systems designed to generate a potentially common phosphoranyl radical intermediate by two different pathways. Both product studies (³¹P or GLC) and product radical ratio determinations (ESR) were carried out on a given reaction system. In no case was a dependence of product oxide ratio on pathway of phosphoranyl radical generation noted. The lack of memory effect can be interpreted (1) in terms of initial formation of a common trigonal bipyramidal phosphoranyl radical with diequatorial ring attachment to phosphorus which then undergoes isomerization to permutamers with apical-equatorial ring prior to β -scission; or (2) by way of rapid equilibration of isomeric forms of the latter intermediate utilizing a rapid mode 4 permutation process. Such an equilibration is consistent with previous ESR measurements reported by another group.

Both ESR^{2,3} and chemical⁴ studies have implicated the probable intermediacy of phosphoranyl radicals, XPZ_3 , in reactions of free radicals with trivalent phosphorus compounds:



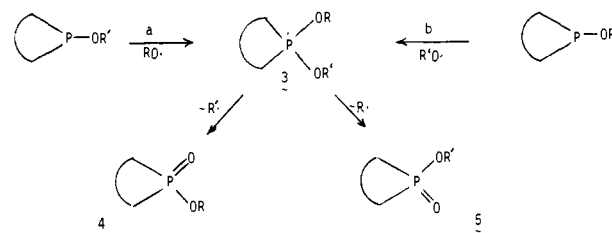
These intermediates are generally assigned a local C_{2v} , near-trigonal-pyramidal (TBP) structure like **1**. (Exceptions occur when one or more phosphorus substituents are aryl.^{3i,j,r,s}) Two substituents are equatorial in the TBP, while two are apical. MO treatments⁶ of these species place the odd electron in an antibonding MO with spin density distributed between phosphorus and the apical ligands as do interpretations of anisotropic ESR data.⁷ When discussing the geometries of phosphoranyl radicals, however, it is convenient to represent the unsubstituted site as in **1**. The odd electron or vacant position thus becomes a phantom ligand and stereochemically significant as an equatorial substituent. No TBP C_{3v} species, **2**, have been identified by ESR in solution.⁵



phoranyl radicals, however, it is convenient to represent the unsubstituted site as in **1**. The odd electron or vacant position thus becomes a phantom ligand and stereochemically significant as an equatorial substituent. No TBP C_{3v} species, **2**, have been identified by ESR in solution.⁵

One may generate a given cyclic phosphoranyl radical by more than one route as in Scheme I. The question then arises

Scheme I



as to whether species **3** is a truly *common* intermediate or whether the observed ratio of product oxides (**4/5**) generated via β -scission may depend on the origin of **3**. TBP structures for **3** may be written with RO and R'O either configurationally equivalent (**6**) or nonequivalent (**7** and **8**). If the rate of β -scission were measurably different at the apical and equatorial sites of **7** and **8** and the latter were neither formed in the same proportions by routes a and b nor rapidly interconverted, then the system of Scheme I would exhibit a so-called *memory effect*. That is, the ratio **4/5** resulting from path a would be different from that formed via path b. We report here the study of several reactions of the type shown in Scheme I. Possible interpretations of the **4/5** ratios found in terms of the geometries of intermediates like **3** and probable permutational isomerization processes available to them are given.

Table I. Product Oxide Ratios

reactant	alkoxy radical	10 oxide/ 9 oxide	12 oxide/ 11 oxide	13 oxide/ 14 oxide	13 oxide/ 15 oxide	% yield
9	<i>t</i> -PentO·	0.88 ± 0.05 (18) ^a				>90
10	<i>t</i> -BuO·	0.91 ± 0.04 (18) ^a				
11	<i>t</i> -PentO·		0.86 ± 0.03 (15) ^a			>90
12	<i>t</i> -BuO·		0.83 ± 0.04 (15) ^a			
13	<i>i</i> -PrO·			0.85 ± 0.03 (11) ^b		
14	<i>sec</i> -BuO·			0.81 ± 0.02 (11) ^b		72-85
15	<i>sec</i> -BuO·				0.59 ± 0.04 (10) ^b	
13	EtO·				0.63 ± 0.03 (10) ^b	63-70

^a By ³¹P NMR. Three integrals per sample. Total number of integrals in parentheses. Error is maximum deviation of a single sample from the mean. ^b By GLC. Total number of samples in parentheses. Error is maximum deviation of a single sample from the mean.

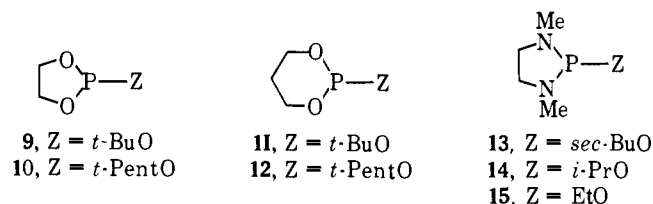
Table II. Radical Ratios by ESR

reactant	alkoxy radical	<i>i</i> -Pr·/ <i>sec</i> -Bu·	<i>t</i> -Bu·/ <i>t</i> -Pent·	<i>T</i> , °C	ref
13	<i>i</i> -PrO·	1.13 ± 0.08 (9) ^c		30	<i>a</i>
14	<i>sec</i> -BuO·	1.18 ± 0.05 (9)		30	<i>a</i>
13	<i>i</i> -PrO·	1.06 ± 0.07 (8)		48	<i>a</i>
14	<i>sec</i> -BuO·	1.04 ± 0.05 (8)		48	<i>a</i>
9	<i>t</i> -PentO·		0.83 ± 0.04	-20	<i>b</i>
10	<i>t</i> -BuO·		0.81 ± 0.04	-20	<i>b</i>
11	<i>t</i> -PentO·		0.73 ± 0.03 (8)	0	<i>a</i>
12	<i>t</i> -BuO·		0.75 ± 0.03 (8)	0	<i>a</i>
11	<i>t</i> -PentO·		0.75 ± 0.02 (8)	20	<i>a</i>
12	<i>t</i> -BuO·		0.77 ± 0.03 (8)	20	<i>a</i>

^a This work. ^b Reference 8. ^c Errors for this work are 1σ standard deviations. Number of replications in parentheses.

Results

A series of trivalent cyclic phosphorus reactants **9–15** was studied. As detailed in Table I, these underwent reaction with the appropriate alkoxy radical to generate the "common" intermediate phosphoranyl radical, **3**. These systems are especially appropriate for such a study since the corresponding phosphoranyl radical has been detected by ESR in all cases.^{2,3} Oxide mixtures corresponding to **4** and **5** were final products. Because of the thermal instability of the corresponding oxides



of **9–12**, analyses of these were made by ³¹P NMR. Otherwise, product ratios and yield were determined by standard GLC methods. Since no other peaks were seen in the ³¹P NMR of the reactions of **9–12**, these reactions are presumed to be near quantitative (>90%). Necessary control reactions were run to ensure that alkoxy radical exchange in the reactants or equilibration of product oxides did not occur. (See the Experimental Section for details.) The irreversibility of alkoxy radical attack in acyclic systems was shown previously.⁴

So that a second measure of product ratios could be made, several of the reactions were run in the cavity of an ESR instrument to determine product radical ratios (R'·/R·). A flow technique was used to maximize the signal. A single peak within each radical signal was chosen for observation (see Experimental Section for details). The ESR investigation of the reaction system involving reactants **9** and **10** was earlier reported by Roberts.⁸ Our product studies of that system furnished an important cross-comparison with the ESR method. Since the radical ratios of Table II reflect steady-state conditions, there is no reason that there need be a close correspondence of product oxide and radical ratio. The latter is

dependent on rates of radical disappearance as well as formation. Although we always attempted to work at low power and modulation amplitudes, these factors can also affect R'·/R·.

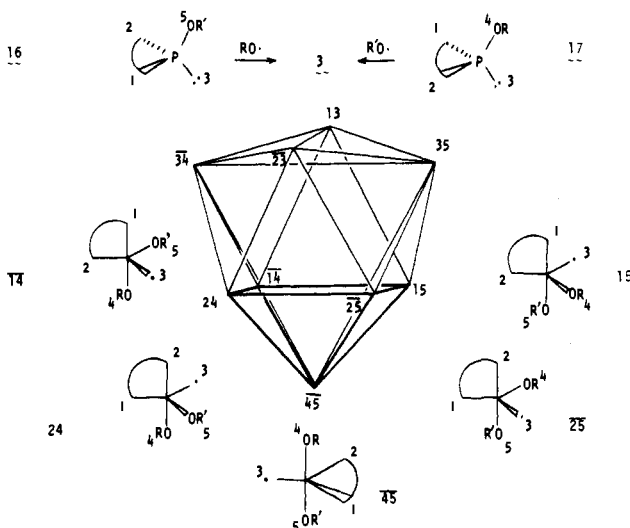
Discussion

The results in Tables I and II demonstrate clearly the lack of any memory in the systems studied of the pathway of formation of the phosphoranyl radical intermediate. Within experimental errors, product ratios from a given reaction pair are the same. The formation of a "common" intermediate leading to memory loss in such reactions could result in several ways.

As stated in the previous section, a lack of memory in these systems might arise because of the equality of β-scission rates for equatorial and apical alkoxy groups on phosphorus. We believe this intuitively to be unlikely. Evidence for a greater rate of apical β-scission is found in very recent kinetic ESR work of Roberts' group^{8b}.

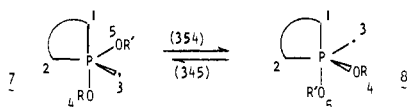
A second possibility is that the attacking alkoxy radical of Scheme I somehow enters apical and equatorial positions randomly to give equal amounts of **7** and **8**. This is unlikely for the following reason. Ab initio calculations for the phosphoranyl radicals PH₄ and PF₄ assign longer bond lengths for apical substituents.^{6a} It follows that such three-center two-electron apical bonds⁷ should be weaker and more readily broken than their equatorial counterparts. Kinetic studies^{3a} of phosphoranyl-radical α-scission strongly suggest a configurational preference for cleavage, presumably apical. Phosphoranyl radical formation by alkoxy radical attack is the microscopic reverse of α-scission and should then occur more readily apical than equatorial. Furthermore, the lowest energy pathway for addition of H· to PH₃ to give PH₄ is that calculated^{6a} for facial attack (apical H introduction) on PH₃. In the related reactions of ROSOR with R'O·, it was clearly shown⁹ that R'O is introduced exclusively apical in the T-shaped radicals, (RO)₂ŠOR', formed. In the arguments which follow, only initial introduction of RO or R'O apical will be considered.

Scheme II



Thirdly, if only radicals of geometry **6** are formed in these reactions, then the lack of memory can be readily understood. All that is required is a rapid averaging of ring conformations to make RO and R'O, which are both apical, completely equivalent. Contrary to this notion is the fact that the only species actually *observed* by ESR during reactions of phosphites like **9** and **10** and their 1,3-oxaza and 1,3-diaza counterparts are those with the five-membered ring attached apical-equatorial to phosphorus^{3e,m,s,t} as in **7** and **8**. In the six-membered ring 1,3-diazaphosphoranyl radical analogues, the same ring attachment is noted.^{3m} The kinetics of β -scission of such intermediates have been studied.^{3d} We will assume that the reaction actually proceeds via the radicals observed.

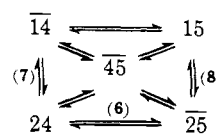
Two further ways in which **7** and **8** could be product-forming intermediates and yet fail to impart a memory to the oxidation process remain as strong possibilities. These require isomerization of initially formed phosphoranyl-radical intermediates prior to β -scission. In previous papers on the stereochemistries of alkoxy-radical oxidations^{4a} and free-radical Arbusov reactions¹ of five- and six-membered ring phosphites like **9**–**12**, it was shown that rapid isomerizations of the intermediate phosphoranyl radicals which involved mode 4 permutations¹⁰ of the substituents on phosphorus prior to or in competition with β -scission were allowed by the overall stereochemistries noted. The elegant studies by Roberts et al. of ESR line shape variation with temperature change present direct evidence for mode 4 isomerizations of five-membered ring species of geometry **7** or **8**.^{3m,s,t} An example of such an isomerization which permutes the positions of the odd electron and nonring substituents and thereby effects the interconversion of **7** and **8** is given below. The particular permutation which involves two



equatorial and one apical substituents can be called an *eea* permutation. The numbers in parentheses designate the exact permutation involved in each direction.

Scheme II is a graphical representation of the formations (via Scheme I) and mode 4 isomerizations of cyclic phosphoranyl radical intermediates.¹¹ The vertices represent the various isomers of **3** and the edges the pathways for interconversion. Structures of five of the intermediates of most interest to this discussion are shown. The numbers assigned to each isomer show which two substituents are apical. The unbarred numbers are for those isomers in which the equatorial substituents are arranged in clockwise ascending numerical order

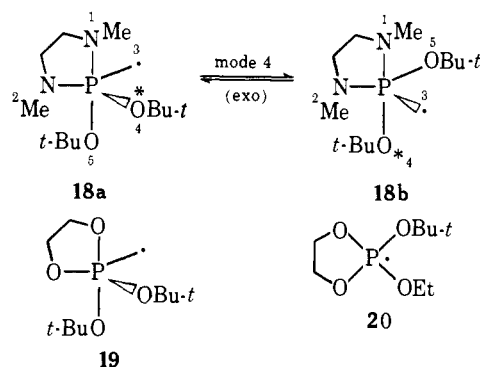
Scheme III



when viewed from the lowest number apical substituent. Only one enantiomer of reactant **16** or **17** is used in Scheme II. To show all 18 isomeric phosphoranyl radicals would require a second diagram as interconversions of barred and unbarred permutamers do not occur via mode 4. However, since the reactants are not themselves chiral, **45** and $\bar{45}$, e.g., are only distinguishable because the ring atoms have been numbered, and $\bar{15}$ and 15 are simply enantiomers. Scheme II is fully sufficient for the arguments which follow. Obviously permutamer $\bar{12}$ with ring attachments both apical is not shown in Scheme II. The isomerizations $\bar{45} \rightleftharpoons 35$, $\bar{45} \rightleftharpoons 34$, and $34 \rightleftharpoons 35$ are included, although the ring appears to make such processes very difficult.

If we exclude as initial intermediates or product-forming ones those isomers with odd electron apical ($\bar{34}$, $\bar{23}$, **13**, and **35**), because they should be of higher energy,^{6a} the relationship between the remaining permutamers is given below (the darkened lines of Scheme II). Permutamer **15** (radical **8**) is an enantiomer of permutamer $\bar{25}$ since the two ring nitrogen or oxygen atoms in **15** and $\bar{25}$ cannot really be distinguished. The same relationships apply to $\bar{14}$ (**7**) and **24**. Quite clearly, if $\bar{45}$ were the intermediate formed initially (as in the earlier consideration) *but* underwent isomerization to $\bar{14}$, **24**, **15**, and $\bar{25}$ before β -scission, no memory effect on the ratio **4**/**5** would be encountered. Reaction in this case would proceed through a truly common, but not product-forming, intermediate. ESR results^{31,m,s,t} fit this scheme.

Exclusive initial formation of $\bar{14}$ (**7**) and **24** from **16** or **15** (**8**) and $\bar{25}$ from **17** also need not result in a memory effect if the equilibrations $\bar{14} \rightleftharpoons 15$ and $24 \rightleftharpoons \bar{25}$ are rapid with respect to β -scission. One cyclic diazaphosphoranyl radical system thoroughly studied kinetically by the Roberts group using ESR techniques is **18**. The isomerization **18a** \rightleftharpoons **18b** has a rate constant^{3m} at 173 K of 10^7 – 10^8 s⁻¹. (This permutation is designated a mode 4 (exo) one as contrasted to a mode 4 (ring) process involving the ring atoms, e.g., $\bar{14} \rightleftharpoons 24$.) For radical



19 the mode 4 (exo) isomerization *k* is about 6×10^9 s⁻¹ at 273 K and about 2×10^7 s⁻¹ at 153 K.^{3u} The E_a estimates for such isomerizations run 3–4 kcal/mol. By contrast E_a for β -scission of *t*-BuOP(OEt)₃, from kinetic measurements, is 7–10 kcal/mol,^{3b,c} and k^{3d} for β -scission of **20** at 213 K is only 0.44 s⁻¹. The lack of memory effect in the cyclic phosphoranyl radicals we have studied is consistent with their relatively slow β -scission rates and rapid mode 4 isomerizations.

A choice between the explanations for the failure of the cyclic systems we have studied to display a memory effect (either initial $\bar{45}$ formation or rapid interconversion of **7** and **8**) awaits experiments with alkoxy groups capable of β -scission

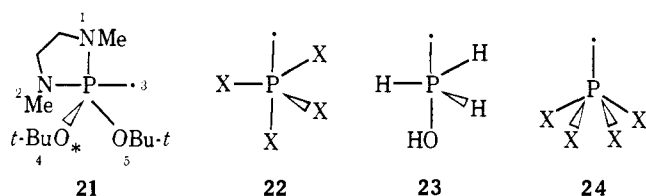
Table III. Physical and Analytical Data for 2-Alkoxy-2-oxo-1,3-dimethyl-1,3,2-diazaphospholanes

RO	bp, ^a °C	molecular formula	calcd			found		
			% C	% H	% P	% C	% H	% P
EtO	73–74 (0.3)	C ₆ H ₁₅ N ₂ O ₂ P	40.44	8.50	17.38	40.26	8.41	17.01
<i>i</i> -Pr	67–68 (0.2)	C ₇ H ₁₇ N ₂ O ₂ P	43.73	8.93	16.11	43.72	8.93	15.71
<i>sec</i> -Bu	79–80 (0.3)	C ₈ H ₁₉ N ₂ O ₂ P	46.58	9.30	15.02	46.44	9.31	15.07

^a Pressures in mmHg in parentheses.

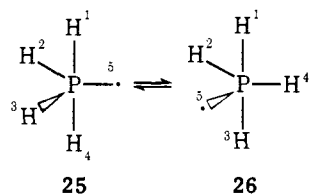
at rates at least competitive with isomerization. PhCH₂O and Ph(CH₃)CHO are possibilities since PhCH₂OP(OC₂H₅)₃ gives PhCH₂· so rapidly that the phosphoranyl radical cannot be detected by ESR.^{3d}

It should be carefully noted that M₄ isomerizations are permutationally equivalent to two successive M₁ steps (M₁ × M₁).¹⁰ Thus the equilibrium **18a** ⇌ **18b** (15 ⇌ 14) can be accomplished via permutamer **21** (23). Ab initio STO-31G



estimates^{6a} place intermediate **22** (X = H or F) 18–20 kcal/mol above the optimized odd electron equatorial TBP geometry. CNDO/2 methods put the energy increase in **23** at only 3.4 kcal/mol above optimum.^{6b} Both approaches make the important prediction that an odd electron as pivot, M₁ pathway via **24** (the barrier species for a true Berry mechanism) should be a much higher energy route. This is by contrast to what is expected for an X₃P species with the odd electron as an electropositive fifth ligand. Such a picture is clearly an oversimplification.

A possible physical mechanism for the M₄ permutation, e.g., **18a** ⇌ **18b** (15 ⇌ 14), is a (TR)² process, originally proposed for X₃P intermediates,²⁰ in part to avoid M₁ pathways involving high-energy intermediates. In fact the calculations of Howell and Olsen^{6a} predict that 120° (TR)²-like physical processes should be the lowest energy pathways (15 kcal/mol barrier) for the isomerization **25** ⇌ **26**. Neither our results nor the variable temperature ESR studies allow one to differentiate between the M₄ permutation and its M₁ × M₁ equivalent much



less to say whether the (TR)² mechanism is operative. The 15 kcal/mol (TR)² barrier and 18–20 kcal/mol required for formation of **22**^{6a} are both much higher than the *E_a*'s for processes like **18a** ⇌ **18b** and the permutations ascribed to ROPX₃ (see below). However, the relative energetics of such processes compared to that for an M₁ permutation via **24** are of the order indicated by ESR^{31,m,s,t} and stereochemistry.^{1,4a}

Previous papers from this laboratory on the stereochemistry of RO· oxidations^{4a} and free-radical Arbuzov reactions¹ involving cyclic phosphoranyl radicals have emphasized that rapid M₁ isomerizations with the odd electron as pivot are relatively slow processes.²¹ That a rapid M₄ permutation of the type **18a** ⇌ **18b** (14 ⇌ 15) is allowed by the stereochemistry observed was also noted.^{1,4a} This conclusion remains. Initial formation and/or interconversion among any of 14, 15, 24, 25, and 45 (Scheme III) as well as product formation from

any of them leaves the overall stereochemistry of the oxidation and radical Arbuzov reactions unaffected. One need only specify that the other intermediates of Scheme II are not accessible or at least do not give products. The same applies to free-radical substitutions at phosphorus.²²

Finally, in an earlier paper on memory effect in noncyclic systems,^{4b} we concluded that any sort of equatorial-apical exchange of alkoxy groups in (RO)₄P· was relatively slow compared to that occurring in (RO)₅P. We have recently experimentally reevaluated certain of these systems using both GLC and ESR methods.²³ Rapid alkoxy exchange is consistent with these more recent results and with variable-temperature ESR results with ROPX₃ systems (X = F,³ⁿ H,^{3f} Me^{3q}). The present view of phosphoranyl radical permutations is that they occur rapidly in both cyclic and acyclic systems, but, as indicated by theory,⁶ ESR,^{31,m,s,t} and stereochemistry,^{1a,4,21} likely by processes permutationally different from those applicable to X₃P.

Experimental Section

Materials. Solvents were spectral grade. Phosphites were shown to be at least 99.7% pure by GLC except for 2-*tert*-butoxy- and 2-*tert*-pentoxy-1,3,2-dioxaphosphorinane, whose purities were checked by ³¹P NMR. Peroxides showed the presence of less than 1% impurities by GLC.

Di-*tert*-pentyl peroxide was prepared by a literature method¹² as were di-*sec*-butyl¹³ diisopropyl,¹³ and diethyl peroxide.¹⁴ **Di-*tert*-butyl peroxide** was commercial material distilled before use.

2-*tert*-Butoxy-1,3,2-dioxaphospholane was prepared according to the method of Lucas et al.,¹⁵ bp 52–53 °C (5 mm) (lit.¹⁵ 73.8 °C (25 mm)), as was **2-*tert*-pentoxy-1,3,2-dioxaphospholane**, bp 63–64 °C (5 mm), δ³¹P 139.1¹⁶ (CDCl₃). The **2-*tert*-butoxy-1,3,2-dioxaphosphorinane** was routinely synthesized by reaction of the corresponding phosphorochloridite¹⁵ with *tert*-butyl alcohol in the presence of Et₃N in ether solution at 0 °C: yield 71%; bp 61–62 °C (4 mm); δ³¹P 126.7¹⁶ (CDCl₃). Anal. Calcd for C₇H₁₅O₃P: C, 47.18; H, 8.50; P, 17.38. Found: C, 46.85; H, 8.45; P, 17.58. In similar fashion the **2-*tert*-pentoxy-1,3,2-dioxaphosphorinane** was prepared: yield 68%; bp 65–66 °C (2 mm); δ³¹P 126.7¹⁶ (CDCl₃). Anal. Calcd for C₈H₁₇O₃: C, 49.98; H, 8.93; P, 16.11. Found: C, 50.05; H, 8.87; P, 16.16.

2-Alkoxy-1,3-dimethyl-1,3,2-diazaphospholanes were prepared in the following manner. To an ice-cooled, stirred solution of 0.26 mol of Et₃N in 500 mL of Et₂O were added dropwise and concurrently 50 mL of Et₂O solutions of the desired ROPCl₂ (0.10 mol) and MeNHCH₂CH₂NHMe (0.11 mol) under nitrogen. Following the addition, the reaction mixture was stirred at room temperature for 24 h. Et₃NH⁺Cl⁻ was removed by filtration, and the solvent was stripped away. Vacuum distillation gave pure product, yields 55–60%. N₂O₄ oxidation¹⁷ in CH₂Cl₂ at 0–5 °C and vacuum distillation yielded pure phosphorodiamidate for analysis and use in GLC sensitivity calibrations. See Table III.

Product Phosphates by ³¹P NMR. A benzene solution about 1.4–1.8 M in peroxide and 0.5 M in phosphite was dispersed in 2.5-mL portions into Pyrex tubes. The samples then were quickly freeze-thaw degassed. One tube was used as a blank while the others were irradiated at room temperature with a 450-W Hanovia medium-pressure UV lamp for 6–7 h. The product phosphate ratios from the dioxaphospholane oxidations were then determined by ³¹P NMR analysis (continuous-wave mode). Three integrations of each sample were made (sweep width 50 Hz, sweep time 250 s) under conditions in which the signals were not saturated. The ratios thus determined on a single sample normally varied over a total range of no more than 2–3%. The dioxaphosphorinane runs were likewise analyzed (with

similar ranges of ratios), but only after removal of volatiles and solvent, and addition of CH_2Cl_2 as solvent to effect resolution of the ^{31}P chemical shifts. In all cases, samples were scanned over a wide range of δ to check for reaction side products. For reaction of each phospholane, two separate sets of three tubes were photolyzed. With the phosphorinanes sets of two and three tubes were photolyzed. Each sample was integrated in triplicate. The errors in Table I give the maximum deviation in either direction of any one ratio from the average of 15–18 integrations.

To standardize the ^{31}P sensitivities, four to five samples containing weighed amounts of the *tert*-butoxy and *tert*-pentoxy-1,3,2-dioxaphospholane or the corresponding 1,3,2-dioxaphosphorinanes in a given solvent were prepared. Following N_2O_4 oxidation of the phosphites,¹⁷ three integrations were made of each sample and the ratios averaged. A plot of mole ratio vs. area ratio was in each case nicely linear and passed through the origin. The slope of the plot was used as correction factor for conversion of area ratio to mole ratio.

Product Studies by GLC. The reactions of the diazaphospholanes were monitored by GLC on a temperature-programmed, Hewlett-Packard 5830A thermal conductivity gas chromatography instrument equipped with digital integrator. Glass columns, 7 ft \times 1/4 in., packed with 4% QF-1 on 80/100 mesh GasChrom Q solid support were used. Trivalent phosphorus compound (~ 0.05 mol/L) and peroxide (~ 0.15 mol/L) along with a weighed quantity of tetradecane as internal standard were dissolved in benzene and the solutions in Pyrex tubes quickly degassed. One sample in each run was analyzed by GLC immediately after mixing to monitor for possible formation of phosphorus oxidation product during the time of sample preparation. Another degassed sample served as a blank and was not analyzed until after completion of the experiment. In no case did the amount of oxide increase in the latter over that found immediately after mixing. The oxide correction was then subtracted from the total found after reaction was completed. This correction ranged from zero with di-*sec*-butyl peroxide to about 1% of the product oxide with diisopropyl peroxide to 10% of product oxide with EtOOEt. On completion of reaction, the tubes were opened and quickly analyzed by GLC. Area ratios were converted to mole ratios using appropriate correction factors derived from sensitivity plots (mole ratio vs. area ratio) using pure phosphorus oxides. All reaction systems were also run to several partial conversions of reactant. Subtraction of the appropriate above correction factor gave the same ratio as that found after total conversion of reactants. Total yields of reactions run to completion were determined from comparisons of product phosphorus oxide areas from alkoxy radical reactions with those obtained on *tert*-butyl hydroperoxide¹⁸ or N_2O_4 ¹⁷ oxidations which are normally near quantitative.

In no case was it possible to see as much as 1% of the trivalent phosphorus compound which could result from transesterification ($\text{R}'\text{O}$ substitution for RO) or reversal of alkoxy addition. Control reactions of **13** with EtO \cdot and *i*-PrO \cdot to which a 10–15% molar excess of **13** oxide was added initially gave a normal product oxide ratio once the initial **13** oxide had been subtracted from that in the final product.

ESR Measurements. A Varian V-4502 X-band spectrometer modified to increase sensitivity by use of a Schottky diode (Sylvania D 5880 A) in a tunable crystal mount, a three-port circulator (Micro-Now Model 506), and low-noise Varian klystron was used. Sample temperature was controlled by a Varian variable-temperature controller and monitored by a Cu–constantan thermocouple. The thermocouple was protected from ultraviolet light exposure and sample contamination by a ceramic cement coating. Sample temperature control was critical in certain cases showing a radical ratio variation with temperature. A modified Dewar insert allowed increased sensitivity through use of 6-mm o.d. Supracil tubing.

The light source was a short-arc, 2500-W Hanovia Hg/Xe super-pressure lamp mounted in an Oriel lamp housing equipped with a collimating quartz lens system. A condensing lens focused the light into the cavity of the spectrometer. Infrared energy emitted by this source was absorbed by an aqueous $\text{Ni}^{2+}/\text{Co}^{2+}$ filter solution.¹⁹

Cyclopentane solutions approximately 2 M in phosphite and 2 M in peroxide were deoxygenated with a helium purge and then flowed through the quartz sample tube at 0.1 mL/min by use of a syringe pump. Microwave power was kept at 17 dB or below in all runs to avoid saturation. A modulation amplitude of 1.25 was employed such that the second-order splittings were broadened just enough that, e.g., the spectrum of the *tert*-butyl radical appeared as ten smooth lines.

Under these conditions the relative spectral line heights, corrected for the fractional intensity of a given line, should be proportional to relative radical concentrations. Care was taken to examine the various spectra for possible overlap of any line chosen for measurement with other radical signals, e.g., those from solvent. The portion of the spectrum containing the lines used was scanned repeatedly under the flow conditions. Peak heights were measured and corrected for fractional intensity, and the relative concentration ratios were subjected to least-squares analysis to obtain an average value and a 1σ standard deviation error limit. The lines used with fractional intensities for various radicals, counting from the first line at lowest field, follow: *i*-Pr \cdot , fifth line (15/128); *sec*-Bu \cdot , fifth line (10/64); *t*-Pent \cdot , eighth line (30/256); and *t*-Bu \cdot , fourth line (84/512).

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