Free-Radical Reactions of Organophosphorus Compounds.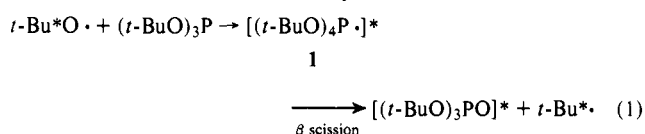 10.[1] Memory Effects in Alkoxy-Radical Oxidations of Trialkyl Phosphites. Alkoxy Group Equivalence in (RO)4P·, a Reexamination

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Abstract: The question of possible memory effects on the alkoxy radical oxidation of trialkyl phosphites has been reexamined using dialkyl peroxides as alkoxy radical sources. Two systems were studied. In each a potentially common phosphoranyl radical was generated by two independent pathways. The phosphoranyl radical, sec-BuOP(OEt)$_3$ or (i-PrO)$_3$POBu-sec, then underwent β scission to yield two trialkyl phosphates in essentially quantitative total amounts. In each case, the product phosphate ratios were determined by GLC analysis. For intermediate sec-BuOP(OEt)$_3$, the relative rates of the two available β scissions were also measured by determining the sec-Bu·/Et· ratio quantitatively by ESR. Neither ESR nor GLC studies revealed a dependence of the β-scission ratio on the pathway of phosphoranyl radical formation. A rapid permutational isomerization which exchanges the alkoxy groups between apical and equatorial positions more rapidly than β scission can occur is proposed as the most reasonable explanation for the failure to find any memory effect in these reactions.

In the past several years there has been a great deal of interest in the configurations and permutational properties of phosphoranyl radicals[2] ($\dot{P}Z_4$), intermediates formed on reaction of a trivalent phosphorus derivative, PZ_3, with a free radical, Z·. Early chemical evidence for the discrete intermediacy of such a species came from a study of the reaction of C-14 labeled *tert*-butoxy radicals with tri-*tert*-butyl phosphite, eq 1.[3] Seventy-five percent of the radioactive label was found in the product phosphate. The apparently random β scission of the four *tert*-butoxy groups in 1 was confirmed in a later ESR study based on examinations of ratios of deuterated and undeuterated *tert*-butyl radicals.[4]

$$t\text{-Bu*O} \cdot + (t\text{-BuO})_3P \rightarrow [(t\text{-BuO})_4P \cdot]*$$

$$\mathbf{1}$$

$$\xrightarrow[\beta \text{ scission}]{} [(t\text{-BuO})_3PO]* + t\text{-Bu*·} \quad (1)$$

Intermediates characterized as tetraalkoxyphosphoranyl radicals are readily identified by ESR in reaction 1[5] and in a number of other similar systems.[6] Rates of β scission of (RO)$_4$P· have been determined by ESR as well. By using substituents which exhibit hyperfine splittings with phosphorus, it has been clearly shown that the Z of $\dot{P}Z_4$ are not configurationally equivalent, and near-trigonal–bipyramidal structures with odd electron or vacant position equatorial are postulated.[7,8]

Formation of a phosphoranyl radical intermediate in which two different alkoxy groups capable of undergoing β scission are attached to phosphorus is shown in eq 2. Two possible

$$\mathbf{2}$$

$$\text{(2)}$$
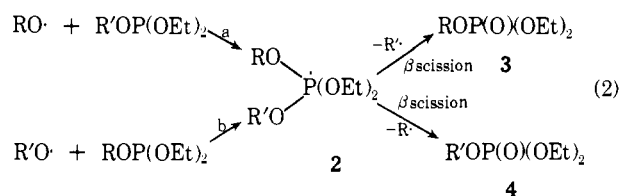
routes to intermediate **2** are given. The trigonal–bipyramidal nature of **2** means that RO and R'O potentially can be in configurationally nonequivalent positions, structures **5** and **6**. Therefore, the product ratio of **3/4** may be dependent on whether **2** is generated by path a or by path b, thus causing the reaction system to display what has been termed[5] a *memory effect*. For this to happen, it is necessary that (1) the rate

constant for β scission be different at the apical, $k_\beta(\text{ap})$, and equatorial, $k_\beta(\text{eq})$, sites; (2) structures **5** and **6**, rather than **7**, be formed in major amounts; (3) intermediates **5** and **6** be

5	**6**	**7**
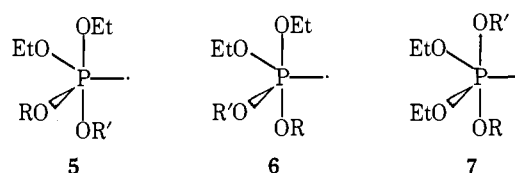
formed in different proportions in pathways a and b; and (4) no rapid randomization of the positions of RO and R'O occur, e.g., **5** $\rightleftarrows$ **6**, ahead of β scission.

Since it seemed possible to us that (t-BuO)$_4$P· (reaction 1) might be a special case in which configurationally nonequivalent *tert*-butoxy groups acidentally underwent apical and equatorial β scission at equal rates, an investigation along the lines depicted in sequence 2 was carried out. The results were reported earlier.[9] Alkoxy radicals with R and R' primary or secondary were generated by thermolysis of the corresponding hyponitrites, RON=NOR and R'ON=NOR'. Product phosphate ratios were determined by GLC techniques. Small but experimentally real memory effects were encountered. From the data, a set of self-consistent k_β values were derived. These showed a reasonable increase in k_β when comparing primary with secondary alkyl-radical formation. Also an expected greater selectivity, as reflected in the ratio $k_\beta(\text{ap})/k_\beta(\text{eq})$, was noted when primary rather than secondary alkyl radicals were formed.

Quite recently, however, a number of ESR results have been published which show clearly that phosphoranyl radicals undergo rapid isomerization reactions which permute the positions of substituents between apical and equatorial sites. Cases studied include the radicals t-BuOPH$_3$,[8d] (EtO)$_2$P(NMe$_2$)$_2$,[8j] ROP̊F$_3$,[8k] ROP̊Me$_3$,[8n] ROP̊MeH$_2$,[8q] and (Me$_2$N)$_2$P̊(OBu-t)Cl.[8q] Rate constants for exchange of 10^6 to 10^7 s^{-1} at ~200 K were encountered. By comparison, the rate constant measured[6b] for β scission of (EtO)$_4$P̊ to form Et· and (EtO)$_3$PO is only 3.6×10^{-1} s^{-1} at 213 K. If (RO)$_4$P· has similar permutation properties, apical–equatorial exchange should greatly exceed the β-scission rate and preclude the possibility of a memory effect. We have, therefore, reinvestigated the memory effect question in two systems, one of which we had examined earlier.

Table I. Product Oxide Ratios by GLC

phosphite	alkoxy radical	T, °C	solvent	$\dfrac{(EtO)_3PO^a}{(EtO)_2P(O)OBu\text{-}sec}$	$\dfrac{(i\text{-}PrO)_3PO^b}{(i\text{-}PrO)_2P(O)OBu\text{-}sec}$
$(EtO)_3P$	sec-BuO·	24	C_6H_6	0.90 ± 0.03 (8)[c]	
$(EtO_2POBu\text{-}sec$	EtO·	24	C_6H_6	0.86 ± 0.03 (8)	
$(EtO)_2POBu\text{-}sec$	EtO·	50	C_6H_6	0.85 ± 0.01 (3)	
$(EtO)_3P$	sec-BuO·	24	C_5H_{10}	0.90 ± 0.01 (2)	
$(EtO)_2POBu\text{-}sec$	EtO·	24	C_5H_{10}	0.88 ± 0.01 (2)	
$(i\text{-}PrO)_3P$	sec-BuO·	24	C_6H_6		0.36 ± 0.01 (3)[c]
$(i\text{-}PrO)_2POBu\text{-}sec$	i-PrO·	24	C_6H_6		0.38 ± 0.01 (3)

[a] Total phosphate yields, 92–100%. [b] Total phosphate yields, 100–106%. [c] Number of samples in parentheses. Error is maximum deviation of value for a single sample from mean. When only two samples were run, error is range of values.

Table II. Product Radical Ratios by ESR

phosphite	alkoxy radical	T, °C	sec-Bu·/Et·
$(EtO)_3P$	sec-BuO·	10	0.75 ± 0.03 (13)[a]
$(EtO)_2POBu\text{-}sec$	EtO·	10	0.76 ± 0.06 (13)
$(EtO)_3P$	sec-BuO·	30	0.96 ± 0.05 (10)
$(EtO)_2POBu\text{-}sec$	EtO·	30	0.99 ± 0.04 (9)

[a] Errors are 1-σ standard deviations. Number of replications in parentheses.

Results

Alkoxy radicals were generated by photolysis of the precursor dialkyl peroxide. These radicals reacted with the appropriate phosphite (Table I) to give the intermediate phosphoranyl radical **2** of eq 2 by two pathways. We were able to easily detect the strong ESR signals of the intermediates $(EtO)_3\overset{.}{P}OBu\text{-}sec$ and $(i\text{-}BuO)_3\overset{.}{P}OBu\text{-}sec$ formed in this study. Both had large isotropic phosphorus hyperfine couplings similar to that of $(EtO)_4P\cdot$.[6b] Ensuing β scission of **2** yielded two phosphates in near-quantitative amounts. The relative amounts of the two β-scission processes occurring in each case were measured. This was done first of all by quantitatively determining by GLC the relative amounts of the two phosphates which resulted. (See Experimental Section for details.) The phosphate ratios are recorded in Table I. Clearly these ratios show no effect of the pathway of phosphoranyl radical generation, solvent, or temperature. Reactions run to partial completion gave no detectable amount (GLC) of the other phosphite which might have resulted from reversible alkoxy-radical addition or transesterification involving small amounts of alcohol potentially formed during photolysis. A further control on the reaction of $(EtO)_3P$ with sec-BuO· was run by adding initially ~15% molar excess of sec-BuOP(O)(OEt)$_2$. No evidence for scrambling of alkoxy groups in the product phosphates under reaction conditions could be found, as a normal product phosphate ratio was obtained once the initial sec-BuOP(O)(OEt)$_2$ had been subtracted from that found at the end of the reaction.

The reactions were also checked for possible formation of phosphates on mixing or standing in the absence of ultraviolet light. These controls and correction terms are described in detail in the Experimental Section. Reactions with diisopropyl and di-sec-butyl peroxides gave essentially negligible phosphate corrections. With EtOOEt peroxide the product phosphate corresponding to reactant phosphite (e.g., sec-BuOP(O)(OEt)$_2$ from sec-BuOP(OEt)$_2$) was reduced 5–7% by the correction. This gave a maximum increase in phosphate ratio, e.g., of from 0.82 to 0.88. With one especially pure sample of this peroxide, the normal ratio was obtained without correction.

To obtain a second measure of the β-scission ratio from the potentially common phosphoranyl radicals formed in each of

the two reaction systems investigated, the product alkyl radicals were studied by ESR. Although for the system involving the radical $(i\text{-}PrO)_3\overset{.}{P}OBu\text{-}sec$ signals assignable to both the isopropyl and sec-butyl radicals were present, it was not possible to obtain sufficient signal intensities, even with a flow system, to accurately determine the ratio i-Pr·/sec-Bu·. However, from the radical $(EtO)_3\overset{.}{P}OBu\text{-}sec$, very reasonable error limits for the ratio sec-Bu·/Et· were attained, as recorded in Table II.

Again the system displays no memory effect. The correspondence between the apparent β-scission competition measured by the two methods is reasonably good, perhaps fortuitiously so. Since the radical ratios reflect steady-state conditions, there is no reason that there need be a close correspondence. Both radical appearance and disappearance rates affect the ratio. Although we always worked at low power and modulation amplitude, these factors also can affect R'·/R·. The temperature effect noted on sec-Bu·/Et· has several possible explanations. E.g., sec-butyl radical spectra are known[10] to display temperature effects as a result of changes in hyperfine couplings with conformer populations. Regardless, at a given temperature and instrument conditions, the ratio of sec-Bu·/Et· is independent of the pathway of formation of the phosphoranyl radical.
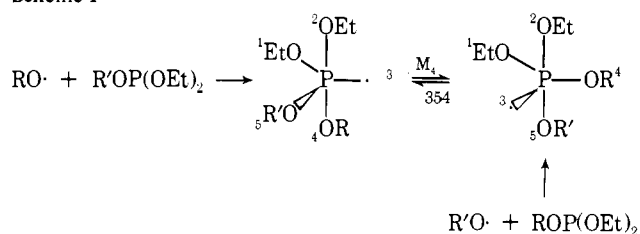
Discussion

The results in Tables I and II demonstrate clearly the lack of any memory of the pathway of formation of the phosphoranyl radical intermediate. These radicals are then truly *common* intermediates in the reaction systems depicted by eq 2. This finding could arise in several ways, one of which we favor.

We must first of all assume that β-scission rates should not be the same for a given alkoxy group when it is attached equatorially to phosphorus as when attached apically. This assumption seems to us intuitively correct. Furthermore, evidence for a greater rate of apical β scission is found in very recent kinetic ESR work of the Roberts group.[11]

It is very unlikely, as well, that intermediate **5** and **6** (or their equivalents) in which the positions of RO and R'O are interchanged apical and equatorial would be formed *initially* in equal amounts on attack by alkoxy radical on phosphite. Ab initio calculations[12] for $\overset{.}{P}H_4$ and $\overset{.}{P}F_4$ assign longer and presumably weaker bonds to the apical substituents. It follows that such apical bonds should be more readily broken than their equatorial counterparts. This preference can be related to the important role of a three-center antibonding orbital in the apical bonding system.[13] Kinetic studies[8n] of phosphoranyl-radical α scission, i.e., $(RO)_2\overset{.}{P}R'_2 \rightarrow (RO)_2PR' + R'$·, strongly suggest a configurational preference for cleavage, presumably an apical one. Phosphoranyl-radical formation by radical attack is the *microscopic reverse* of α scission and should then occur more readily apical than equatorial. For addition of H· to PH$_3$ to form $\overset{.}{P}H_4$, the calculated lowest energy pathway is

Scheme I

$$RO\cdot + R'OP(OEt)_2 \longrightarrow \begin{array}{c} {}^2OEt \\ {}^1EtO \diagdown \mid \\ P\!\!-\!\!\cdot \\ {}^5R'O \diagup \mid {}_4OR \end{array} \quad {}_3 \underset{354}{\overset{M_4}{\rightleftharpoons}} \quad \begin{array}{c} {}^2OEt \\ {}^1EtO \diagdown \mid \\ {}_3 \diagup P\!\!-\!\!OR^4 \\ {}_5OR' \end{array}$$

$$\uparrow$$

$$R'O\cdot + ROP(OEt)_2$$

that for facial attack on PH_3 (apical H introduction).[12] It was clearly shown[14] that in the oxidative addition of $R'O\cdot$ to ROSOR the R'O is introduced exclusively apical in the T-shaped radicals, $(RO)_2SOR'$, formed. In the discussion which follows, only initial introduction of RO or R'O apical will be considered.

Reaction entirely by way of initial **7** formation followed by β scission obviously would give the results encountered in our study. However, random introduction of attacking alkoxy opposite one of the three groups on phosphorus would give **7** only $\frac{1}{3}$ of the time. The thermodynamic preference, if any, is for a larger and also less electronegative alkoxy group to be equatorial.[8j,q] A kinetic parallel would favor $EtO\cdot$ attack on *sec*-BuOP(OEt)$_2$ to give an intermediate with *sec*-BuO equatorial rather than apical as needed for identical phosphoranyl radicals (**7**) to be formed by the two pathways. Thus there is no reason why intermediate **7** should be formed exclusively.

The most plausible reason for the lack of memory found in these systems is a rapid permutational isomerism which randomizes apical and equatorial substituents. For such apical-equatorial exchanges in cyclic systems, a mode 4 (M_4) (Musher notation[15]) permutation is proposed.[8j,p,q] This permutation, applied to the noncyclic phosphites in question, is shown in Scheme I. The representation of the odd electron as a fifth ligand may not be an accurate description of the electron structure of such species.[12,13,16] It is, however, a stereochemically useful concept and allows one to see the permutation as involving the odd electron (or vacant position) and two alkoxy groups. Other mode 4 permutations involving three alkoxys could accomplish the same thing. As noted earlier, apical-equatorial exchange of a wide range of groups attached to phosphorus has been noted for noncyclic phosphoranyl radicals, at rates much greater than those for β scission. There is no reason to expect tetraalkoxy phosphoranyl radicals to be permutationally different. The failure to find a memory effect in the systems studied here is entirely consistent with this expectation.

It should be noted, as well, that no specific mode of equatorial-apical ligand exchange can be assigned to the line-shape effects noted for the noncyclic phosphoranyl radicals studied to date. Furthermore, the overall mode 4 isomerization of Scheme I can be accomplished by two mode 1 steps (the mode of the familiar Berry[17] and turnstile[18] mechanisms of truly pentacovalent phosphorus systems) with an odd-electron-apical species as a transient, higher energy intermediate. Alternately a $(TR)^2$ mechanism[18] could be operative. Calculations suggest that both of these may be *relatively* low energy processes.[12,16] (See discussion in preceding paper.[1b])

Taken together, the evidence from stereochemical work,[1a] temperature dependent ESR studies,[8d,j,k,n,p,q] and chemical[1b] and ESR investigations[1b,11] of memory effects on $RO\cdot$ oxidations indicates that permutations of substituents about phosphorus in phosphoranyl radicals occur rapidly. From experimental evidence in cyclic systems it appears that the most rapid *overall* mode of ligand exchange is M_4. This is also consistent with the predictions of MO calculations for noncyclic $X_4P\cdot$.[12,16] Whether the overall M_4 occurs in one step or by successive mode 1 processes via intermediates with odd electron apical,

such permutational behavior is contrary to what is predicted if one views phosphoranyl radicals as being essentially pentacovalent phosphorus analogues with the odd electron as an electropositive ligand. The latter is obviously an unjustified oversimplification when one considers the electronic structure[12,13,16] of $X_4P\cdot$. Theoretical reasons why $X_4P\cdot$ should have permutational properties different from X_4S as well have also been given.[12]

In the earlier work in which memory effects were encountered,[9] the alkoxy radical sources were primarily dialkyl hyponitrites. A number of controls to attempt to assure that all the product phosphate came from alkoxy radical oxidation were run. These included using both thermal and photodecompositions and using several independently prepared samples of hyponitrites at varying concentration levels. The kinetics of thermal decomposition of the hyponitrites in the presence of added phosphite were also studied to ensure that some sort of induced decomposition of hyponitrite was not involved. Unfortunately, the dialkyl hyponitrites are oils and liquids and not distillable. In addition, one cannot check by GLC for oxidation following mixing of reactants as in the studies with dialkyl peroxides because of the thermal instability of the hyponitrites. It now appears that the apparent memory effects in the earlier work arose from unaccounted for oxidation processes accompanying the normal alkoxy radical processes. These oxidations coincidentally gave trends correlatable with radical stability changes.

Experimental Section

The peroxides, diethyl,[19] diisopropyl,[20] and di-*sec*-butyl,[21] were prepared according to published procedures and after distillation were all better than 98% pure by GLC analysis. $(EtO)_3P$ and $(i\text{-}PrO)_3P$ were commercial samples, carefully distilled to >99% purity (GLC) before use. The phosphorodichloridite *sec*-BuOPCl$_2$,[21] prepared from the alcohol and PCl$_3$ at ice temperature, was reacted with ethanol or isopropyl alcohol in the presence of Et$_3$N to give >99% pure (GLC) *sec*-BuOP(OEt)$_2$ (bp 72–73 °C at 14 mm, lit.[22] 68–69 °C at 12 mm) and $(i\text{-}PrO)_2POBu\text{-}sec$ (bp 78–79 °C at 11 mm). Preparation of these phosphites in *n*-pentane rather than Et$_2$O solvent and final distillation from CaH$_2$ ensured that scrambling of the alkoxy substituents did not occur.

Product Studies by GLC. Reactions were monitored on a temperature-programmed, Hewlett-Packard 5830A thermal conductivity gas chromatograph equipped with electronic digital integrator. Glass columns, 7 ft by $\frac{1}{4}$ in., packed with 4% QF-1 on 80–100 mesh Gas-Chrom Q solid support, were used. Photolyses were run for 5–6 h using a 450-W Hanovia medium-pressure Hg lamp. Reaction tubes were suspended in a water bath during photolysis.

Phosphite (~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 were quickly freeze–thaw degassed. One sample in each run was analyzed by GLC immediately after mixing to monitor for possible formation of phosphate 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 phosphate increase in the latter over that found immediately after mixing. Only phosphate corresponding to the starting phosphite was formed. The oxide correction was then subtracted from the total found in each completed reaction. This correction, based on product phosphate, amounted to <1% with diisopropyl peroxide, 0–3% with di-*sec*-butyl peroxide and 5–7% with diethyl peroxide. With one sample of apparently especially pure diethyl peroxide, a correction of <1% was required. Oxide ratios equal to the corrected ones in other runs were found. If the reaction tubes were left open to the air before analysis, the amount of phosphate from the starting phosphite was gradually increased. Therefore, reactions were run either to complete consumption of phosphite or were analyzed *immediately* after opening each tube under nitrogen.

Yields and product phosphate ratios for the reactions giving $(EtO)_3PO$ and *sec*-BuOP(O)(OEt)$_2$ were calibrated using standard samples of pure phosphate obtained by N_2O_4 oxidation[23] of starting phosphite followed by distillation to >99% purity. Plots of mole ratio vs. area ratio were employed. In both systems total phosphate yield

was determined by *t*-BuOOH oxidation[24] (normally quantitative) of a blank solution of starting phosphite and tetradecane internal standard. The area ratio of phosphate to tetradecane in the blank was compared with the area ratio of the sum of the two product phosphates to internal tetradecane in the alkoxy-radical oxidations. In the reactions giving $(i\text{-PrO})_3PO$ and $(i\text{-PrO})_2P(O)OBu\text{-}sec$, area ratios were not corrected for small differences in phosphate sensitivities (9% in the comparison of $(EtO)_3PO$ vs. $sec\text{-BuOP}(O)(OEt)_2$). The yield in these cases, 100–106%, is comparable with those determined with sensitivity calibrations, 92–100%. Reactions in cyclopentane were carried out in the same way.

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 kystron was used. Sample temperature was controlled by a Varian variable-temperature controller and monitored by a copper 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 samples in 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 lense system. A condensing lense focused the light into the cavity of the spectrometer. Infrared energy emitted by this source was absorbed by an aqueous Ni^{2+}/Co^{2+} filter solution.[25] Cyclopentane solutions 2 M in phosphite and 2 M in peroxide were deoxygenated with a helium purge and then allowed to flow 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 125 was employed such that signals were broadened just enough to remove second-order splittings. 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, corrected for fractional intensity, and the relative concentration ratios subjected to least-squares analysis to obtain an average value and a $1\text{-}\sigma$ standard deviation error limit. The lines used with fractional intensities for various radicals, counting from the first line at lowest field were as follows: Et·, fifth line (16/32), and *sec*-Bu·, fifth line (10/64).

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