

Phosphadioxirane Intermediates in the Reaction of Singlet Oxygen with Phosphites and Phosphines

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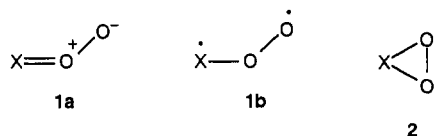
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Intermediates in the singlet oxygen reaction of phosphites and phosphines have been studied by trapping and tracer experiments. Trapping study with diphenyl sulfoxide revealed that the added substrate and phosphite are competing toward the same intermediate. The relative reactivity of $(\text{BuO})_3\text{P}/\text{Ph}_2\text{S}/\text{Ph}_2\text{SO} = 300:4:1$ and the negative ρ -value of -0.63 for diphenyl sulfoxides are not consistent with 1,3-dipolar phosphine peroxides, but suggest electrophilic O-transfers by cyclic phosphadioxiranes. Intermediacy of phosphadioxiranes was supported by an ^{18}O -tracer study on the formation of rearranged diphenylphosphinate from $^1\text{O}_2$ and triphenylphosphine. Theoretical calculations also supported the dioxirane intermediate by predicting no existence of 1,3-dipolar peroxide.

Introduction

Much attention has been concentrated on oxygen-atom transfers by dioxiranes¹ and carbonyl oxides.² Carbonyl oxides are known to be intermediates in the reaction of olefins with ozone,^{3a} and of diazo compounds with singlet oxygen.^{3b} The most characteristic reaction of carbonyl oxides is a nucleophilic oxygen transfer, (i.e., the relative substrate reactivity of $\text{Ph}_2\text{SO} > \text{Ph}_2\text{S}$)^{4,5} indicating the importance of dipolar structure 1a ($\text{X} = \text{R}_2\text{C}$). Dioxiranes



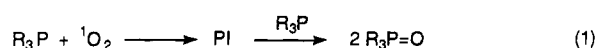
(2, $\text{X} = \text{R}_2\text{C}$), produced from ketones and monoperoxy-sulfate, are recently revealed to be isolable and to react efficiently as a typical electrophilic oxidant.^{1,6} These facts indicate that carbonyl oxides and dioxiranes are different species and not interconvertible with each other. For the case of persulfoxides (1, $\text{X} = \text{R}_2\text{S}$), the dipolar structure 1a is of importance,⁷ their characteristic reaction again being nucleophilic O-transfers.^{8a} In contrast, nitroso

oxides, formed from nitrenes and oxygen, have been regarded as a diradical O-transferring agent (1b, $\text{X} = \text{RN}$).⁹

In relation to reactions of carbonyl oxides, persulfoxides, and nitroso oxides, we became interested in the reactivity of phosphine peroxides, e.g., 1 or 2 with $\text{X} = \text{R}_3\text{P}$. The singlet oxygen oxidation of phosphites was reported to give phosphates in good yields¹⁰ and recently the quenching rates by phosphites have been determined directly.¹¹ However, nothing has been known on the structure and reactivity of peroxidic intermediates (PI) involved. Herein, we report that the intervention of cyclic phosphadioxiranes (2, $\text{X} = \text{R}_3\text{P}$) is suggested by trapping and ^{18}O -tracer experiments in the photooxidation of phosphites and phosphines.

Results

Trapping of Intermediates in the Reaction of Tributyl Phosphite (3) and Singlet Oxygen. The reaction of singlet oxygen with trialkyl phosphites is known to afford the corresponding phosphates in high yields.¹⁰ The intervention of singlet oxygen in this reaction was evidenced by an effective inhibition by β -carotene as a typical $^1\text{O}_2$ quencher. Recently, the quenching rate of $^1\text{O}_2$ by trimethyl phosphite has been directly determined to be $(3-6) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$.¹¹ Nothing has, however, been known on the intermediates involved in the $^1\text{O}_2$ oxidation of trivalent phosphorus compounds R_3P . By analogy with the case of sulfides,^{7,8} a possible pathway for the $^1\text{O}_2$ oxidation of R_3P is eq 1 involving peroxidic intermediate (PI).



Trapping experiments were undertaken in order to characterize the reactivity of PI in the reaction of tributyl phosphite (3) with singlet oxygen. Irradiation at over 400 nm of 5–20 mM phosphite 3 and 0.1 mM Methylene Blue (MB) in acetonitrile under oxygen afforded ~90% yields of tributyl phosphate (run 1 in Table I). When 10 vol%

(1) (a) Murray, R. W. *Chem. Rev.* 1989, 89, 1187. (b) Adam, W.; Curci, R.; Edwards, J. O. *Acc. Chem. Res.* 1989, 22, 205.

(2) (a) Sander, W. W. *Angew. Chem., Int. Ed. Engl.* 1990, 29. (b) Bunelles, W. H. *Chem. Rev.* 1991, 91, 335.

(3) (a) Pailey, P. S. *Ozonation in Organic Chemistry*; Academic Press: New York, 1978, 1982; Vols 1 and 2. (b) Highly, D. P.; Murray, R. W. *J. Am. Chem. Soc.* 1974, 96, 3330.

(4) This point was verified by the fact that carbonyl oxides can transfer oxygen atom to sulfoxides (e.g., Ph_2SO) more efficiently than the corresponding sulfides (Ph_2S), the relative reactivity being $\text{Ph}_2\text{SO} > \text{Ph}_2\text{S}$. See, for example, ref 5.

(5) (a) Sawaki, Y.; Kato, H.; Ogata, Y. *J. Am. Chem. Soc.* 1981, 103, 3832. (b) Pryor, W. A.; Gorindam, C. K. *J. Am. Chem. Soc.* 1981, 103, 7681. (c) Adam, W.; Hass, W.; Sieker, G. *J. Am. Chem. Soc.* 1984, 106, 5020.

(6) (a) Edwards, J. O.; Pater, R. H.; Curci, R.; Furia, F. D. *Photochem. Photobiol.* 1979, 30, 63. (b) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* 1985, 50, 2847. (c) Cassidei, L.; Fiorentino, M.; Mello, R.; Sciacovelli, O.; Curci, R. *J. Org. Chem.* 1987, 52, 699.

(7) (a) Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* 1971, 93, 3795. (b) Liang, J.-J.; Gu, C.-L.; Kacher, M. L.; Foote, C. S. *J. Am. Chem. Soc.* 1983, 110, 494.

(8) (a) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* 1981, 103, 5947. (b) Watanabe, Y.; Kuriki, N.; Ishiguro, K.; Sawaki, Y. *J. Am. Chem. Soc.* 1991, 113, 2677.

(9) (a) Sawaki, Y.; Ishikawa, S.; Iwamura, H. *J. Am. Chem. Soc.* 1987, 109, 584. (b) Ishikawa, S.; Tsuji, S.; Sawaki, Y. *Ibid.* 1991, 113, 4282.

(10) Bolduc, P. R.; Goe, G. L. *J. Org. Chem.* 1974, 39, 3178.

(11) Nahm, K.; Foote, C. S. *J. Am. Chem. Soc.* 1989, 111, 1909.

Table I. Trapping of Intermediates in the $^1\text{O}_2$ Reaction of $(\text{BuO})_3\text{P}$ in MeCN^a

run	$(\text{BuO})_3\text{P}$, mM	additive	conversion, %	product, % ^b	
				$(\text{BuO})_3\text{P}=\text{O}$	others
1	20	—	90	94	—
2	20	10% PhH	100	90	none
3	5	0.1 M Ph_2S	68	80	Ph_2SO , 8
4	2	0.1 M Ph_2SO	100	88	Ph_2SO_2 , 11
5	5	0.1 M Ph_2SO	96	81	Ph_2SO_2 , 5
6 ^c	5	0.05 M Ph_2SO	38 ^c	92	Ph_2SO_2 , 2.3
7 ^c	5	0.05 M $\text{Ph}_2\text{SO}/10\%$ MeOH	36 ^c	73 ^d	Ph_2SO_2 , 2.1

^a Irradiation of 0.1 mM Methylene Blue and 2–20 mM $(\text{BuO})_3\text{P}$ at >400 nm (5% NaNO_2 filter, 300-W medium pressure Hg lamp) for 1 h in O_2 -saturated MeCN. The photooxidation of Ph_2S and Ph_2SO in the absence of $(\text{BuO})_3\text{P}$ was negligible (i.e., $<0.1\%$) under the reaction conditions. ^b Products yields were determined by GLC and based on the phosphite consumed. The values are the mean of two determinations which were within $\pm 5\%$ from the means. ^c Irradiation time: 10 min. ^d Dibutyl methyl phosphite was also detected.

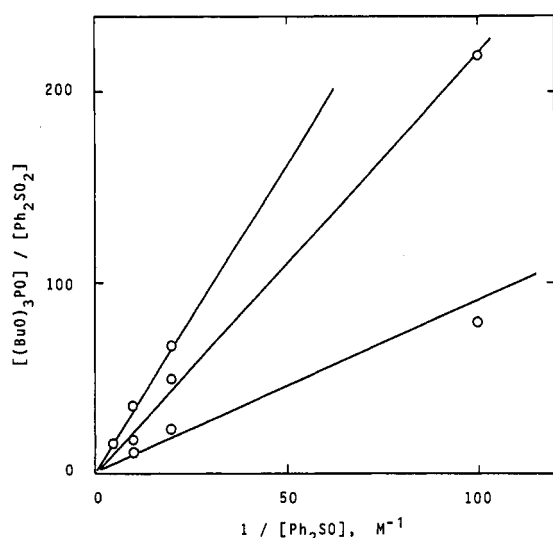
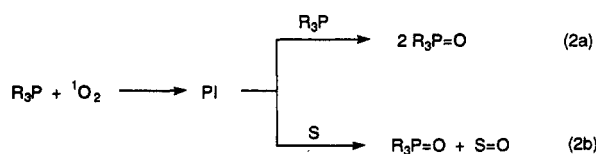


Figure 1. Sulfoxide trapping of PI in the reaction of $^1\text{O}_2$ and $(\text{BuO})_3\text{P}$ in MeCN : slope 4.9, 3.1, and 1.4 for 10, 5, and 2 mM $(\text{BuO})_3\text{P}$, respectively. For experimental details see footnote a of Table I.

benzene (run 2) or cyclohexane was added, the hydroxylation of these substrates was not observed. The addition of diphenyl sulfides or sulfoxides, which are insensitive to singlet oxygen, resulted in oxygen-atom transfer to the sulfur substrates (runs 3 and 4). The O-transfer to the sulfoxide decreased with increasing relative concentration of phosphite 3 (cf. runs 4–6).

The reciprocal plots of relative product yields and $[\text{Ph}_2\text{SO}]$ in Figure 1 indicate that $(\text{BuO})_3\text{P}$ and Ph_2SO are reacting competitively with the same intermediate according to eq 2, where S is an added substrate. The analysis



of the trapping kinetics is just as reported for the $^1\text{O}_2$ reaction of sulfides,^{7b} and the resulting slopes in Figure 1 afford the relative reactivity of $(\text{BuO})_3\text{P}/\text{Ph}_2\text{SO} = 300:1$. The high reactivity of phosphite has also been reported

Table II. Relative Reactivity of Substrates during the $^1\text{O}_2$ Reaction of $(\text{BuO})_3\text{P}$ and Ph_3P^a

R_3P	substrates	relative reactivity ^b
$(\text{BuO})_3\text{P}$	Ph_2SO	(1.0)
	$(p\text{-MeOC}_6\text{H}_4)_2\text{SO}$	2.8
	$(p\text{-MeC}_6\text{H}_4)_2\text{SO}$	1.7
	$(p\text{-ClC}_6\text{H}_4)_2\text{SO}^c$	0.63
	$(p\text{-MeC}_6\text{H}_4)_2\text{S}$	6.1
Ph_3P	Ph_2SO	(1.0)
	$(p\text{-MeC}_6\text{H}_4)_2\text{S}$	6.0

^a 50 mM each of Ph_2SO and substrate were added in the acetonitrile solution of R_3P (5–10 mM) and MB (0.1 mM); irradiated for 1 h at >400 nm under oxygen. ^b Relative reactivities ($\pm 5\%$) were calculated from the relative yields in competitive reactions using Ph_2SO as a reference substrate. Conversions of substrates were below 2% for each run. ^c Reaction in $\text{MeCN}-\text{CH}_2\text{Cl}_2$ (4:1); CH_2Cl_2 was added to dissolve the sulfoxide. The solvent effect was assumed to be negligible since the relative reactivity of $(p\text{-MeC}_6\text{H}_4)_2\text{SO}$ was of the same value in the presence and absence of 25% CH_2Cl_2 .

for trapping intermediates in the photooxidation of sulfides¹¹ and is comprehensible since trivalent phosphites are known as effective deoxygenating agents.¹²

The comparison of runs 6 and 7 in Table I shows that the photooxidation of phosphite 3 was not affected by adding 10% methanol. This fact suggests that the PI is not affected by protic solvents, which is quite contrasted to the dramatic accelerating effect of alcohols in the $^1\text{O}_2$ oxidation of sulfides.^{7,8,13} A small amount of dibutylmethyl phosphite was obtained which was formed probably via the secondary dark reaction of tributyl phosphite with solvent methanol.¹⁴

Relative reactivities of substituted diphenyl sulfoxides were determined by competitive trappings with equal amounts of two substrates. The resulting substituent effect was in the ratio of $p\text{-MeO}/p\text{-Me}/p\text{-Cl} = 2.8:1.7:1.0:0.63$ as listed in Table II. The plot of logarithm of relative rates vs Hammett's σ -values affords a negative ρ -value of -0.63 (correlation coefficient $r = 0.982$). The data in Table II also show that diphenyl sulfides are more reactive than the corresponding sulfoxides, the relative rate of $\text{Ar}_2\text{SO}/\text{Ar}_2\text{S}$ being 1:3.6 for $\text{Ar} = p\text{-MeC}_6\text{H}_4$. The negative ρ -value and relative reactivity of $\text{Ar}_2\text{S} > \text{Ar}_2\text{SO}$ suggest that the PI transfers oxygen atom electrophilically, which is in sharp contrast to the reported cases of carbonyl oxides⁵ and persulfoxides.^{7,8}

Trapping and ^{18}O -Tracer Study in the $^1\text{O}_2$ Oxidation of Triphenylphosphine (4). Triphenylphosphine (4) reacted similarly with singlet oxygen to yield triphenylphosphine oxide in high yields (Table III). In this reaction system, cyclohexane (run 9 in Table III) and benzene were not oxidized, but O-transfers to Ph_2SO and Ar_2S occurred although in low efficiency. Since the O-transfer to these substrates was more effective when the initial concentration of 4 was lower (cf. runs 10 and 11), it is apparent that Ph_3P and added substrates are competing toward the same PI. Diaryl sulfide was more reactive than diaryl sulfoxide, the relative reactivity of $(p\text{-MeC}_6\text{H}_4)_2\text{S}/\text{Ph}_2\text{SO}$ being 6.0 (means of runs 10 and 11 in Table III), which is just the same with the previous case

(12) (a) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; John Wiley and Sons: Inc.: New York, 1967; Vol. 1, p 1212. (b) Smith, O. J. H. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Ed.; Pergamon Press: Oxford, 1979; Vol. II, p 1154.

(13) Clennan, E. L.; Yang, K. *J. Am. Chem. Soc.* 1990, 112, 4044.

(14) A control experiment of tributyl phosphite in the presence 10% MeOH resulted in the formation of a small amount of dibutyl methyl phosphite probably via the secondary dark reaction of tributyl phosphite with solvent methanol.

Table III. Products from the Reaction of Ph_3P with $^1\text{O}_2^a$

run	Ph_3P	additive	conversion, %	products (%) ^b	
				$\text{Ph}_3\text{P}=\text{O}$	others
8	10	-	>99	98	$\text{Ph}_2\text{P}(\text{O})\text{OPh}$, 0.9
9	10	5% C_6H_{12}	>99	>99	none ^{c,d}
10	5	$\text{Ph}_2\text{SO}/\text{Ar}_2\text{S}^e$	>99	>99	$\text{Ar}_2\text{SO}/\text{Ph}_2\text{SO}_2$, ~1 (6.5:1 ratio)
11	10	$\text{Ph}_2\text{SO}/\text{Ar}_2\text{S}^e$	>99	98	$\text{Ar}_2\text{SO}/\text{Ph}_2\text{SO}_2$, <1 (5.4:1 ratio)
12	2	-	>99	98	$\text{Ph}_2\text{P}(\text{O})\text{OPh}$, 1.3
13	20	-	>99	99	$\text{Ph}_2\text{P}(\text{O})\text{OPh}$, 0.6

^a See footnote a in Table I. ^b Products were determined by GLC and based on the phosphine consumed. ^c Cyclohexanol and cyclohexanone were not detected (i.e., <0.5%). ^d $\text{Ph}_2\text{P}(\text{O})\text{OPh}$ was not determined. ^e 50 mM each of Ph_2SO and (*p*- MeC_6H_4) $_2\text{S}$ were added ($\text{Ar}_2\text{S} = (\text{p-MeC}_6\text{H}_4)_2\text{S}$).

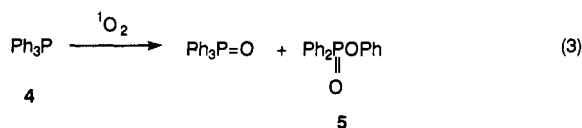
Table IV. ^{18}O -Tracer Study on the Formation of Phenyl Diphenylphosphinate (5) from Ph_3P and $^{18}\text{O}_2$

run	conditions ^a	product	mass spectra ^b		
			M	M + 2	M + 4
		Observed			
14	20 mM $\text{Ph}_3\text{P}/^{18}\text{O}_2^c$	$\text{Ph}_2\text{P}(\text{O})(\text{OPh})$	100	11.8	5.9
15	20 mM $\text{Ph}_3\text{P}/\text{O}_2^d$	$\text{Ph}_2\text{P}(\text{O})(\text{OPh})$	100	10.5	0.3
		difference ^e	100	1.3	5.6
		Calculated			
	retention/ scramble ^f		100	0.5	6.2
			100	3.6	0.0

^a See footnote a in Table I for conditions. ^b Mass spectral data for $\text{Ph}_2\text{P}(\text{O})(\text{OPh})$, M = 294. The observed values are the means of two determinations. ^c Oxygen gas: $^{32}\text{O}_2/^{34}\text{O}_2/^{36}\text{O}_2 = 100:0.5:6.2$. ^d Control experiment using natural oxygen gas under the same conditions. ^e Net values for ^{18}O -contents. ^f Calculated for M + 2 and M + 4 components according to eqs 4 and 5, respectively.

of $(\text{BuO})_3\text{P}$. This indicates that similar intermediates are involved in the $^1\text{O}_2$ reaction of Ph_3P and $(\text{BuO})_3\text{P}$.

Another interesting point is that the $^1\text{O}_2$ reaction of Ph_3P afforded rearranged phenyl diphenylphosphinate (5) although in small amounts. The yields of 5 were reduced when the concentration of 4 was higher (cf. runs

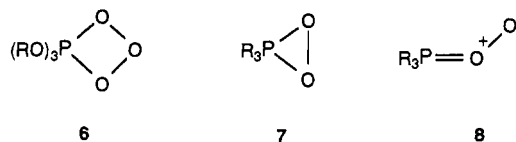


12 and 13). This fact indicates that the precursor of rearrangement is competitively trapped by 4. An ^{18}O -tracer experiment was carried out in order to choose a unimolecular or bimolecular rearrangement. Mass spectral data were obtained for phosphinate 5 produced in the photooxidation with oxygen gas involving 6.2% $^{18}\text{O}_2$. The resulting data in Table IV show that the M + 4 component in 5 was retained almost completely. That is, the two oxygen atoms in starting O_2 gas are introduced in one phosphinate molecule, supporting the unimolecular rearrangement.

Discussion

The adducts of phosphites and ozone are stable at low temperature as a four-membered cyclic peroxide (6) and have been utilized as an $^1\text{O}_2$ precursor.¹⁵ As far as we know, nothing is known for an adduct of phosphites with

oxygen. Jenkins et al.¹⁶ reported on a reaction of triphenylphosphine with diethyl azodicarboxylate and hydrogen peroxide. The major product was phosphinate 5 which was reported to be produced either *via* three-membered peroxide 7 or six-membered cyclic dimer of dipolar peroxide 8.



The present study was carried out to characterize, mostly by trapping experiments, peroxidic intermediates (PI) in the reaction of trivalent phosphorus compounds with singlet oxygen. The characteristic features of PI involved are as follows. (a) Relative reactivities of substrates are $(\text{BuO})_3\text{P}/\text{Ph}_2\text{S}/\text{Ph}_2\text{SO} = 300:4:1$. (b) A negative ρ -value of -0.63 was obtained for substituted diphenyl sulfoxides. (c) Benzene and cyclohexane were not hydroxylated. (d) Methanol was of practically no effect. (e) A tracer study on the rearranged phosphinate 5 from Ph_3P suggested a unimolecular rearrangement. On the basis of these findings the structure and reactivity of PI involved are discussed in the following.

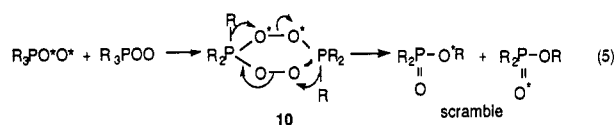
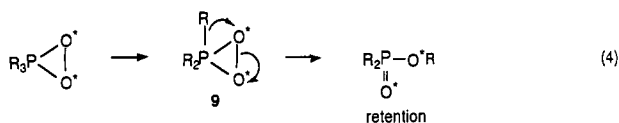
Reactivity and Structure of PI. Two structures, phosphadioxiranes 7 and/or 1,3-dipolar phosphine peroxide 8, are conceivable for peroxidic intermediates in the reaction of trivalent phosphorus compound R_3P and $^1\text{O}_2$. The electrophilic nature of PI involved is clearly suggested by the relative reactivity of $\text{Ph}_2\text{S} > \text{Ph}_2\text{SO}$ and the negative ρ -value of -0.63 for Ar_2SO . This feature is contrasted to the reported cases of carbonyl oxides⁵ and persulfoxides^{8a} where the 1,3-dipolar structures 1a are most important and transfer O-atoms nucleophilically (i.e., $\text{Ph}_2\text{SO} > \text{Ph}_2\text{S}$ and $\rho > 0$ for Ar_2SO). This consideration strongly suggests that in the present reaction of R_3P and $^1\text{O}_2$ the 1,3-dipolar species such as 8 is not involved and phosphadioxirane intermediates 7 are more probable.

Practically no effect of methanol for the $^1\text{O}_2$ reaction of R_3P also indicates the unimportance of 1,3-dipolar 8. This is because the stability and reactivity of 1,3-dipolar peroxides 1a such as carbonyl oxides^{5a} and persulfoxides^{7,8} are known to be affected significantly by adding methanol. Since cyclohexane and benzene were not hydroxylated during the reaction of R_3P and $^1\text{O}_2$, diradical structure 1b ($\text{X} = \text{R}_3\text{P}$) is not important. The electrophilic nature and no effect of methanol are well explained by phosphadioxirane 7 since the electrophilic nature of cyclic dioxiranes (2, $\text{X} = \text{R}_2\text{C}$) is thoroughly documented.¹

Phosphadioxirane Intermediates. As stated above, the trapping experiments suggest that the structure of PI is probably cyclic phosphadioxirane 7 rather than the dipolar 1a or diradical structure 1b. Is there another supporting evidence? One evidence, although not direct, is the ^{18}O -tracer experiment for rearranged product 5 from triphenylphosphine. Two plausible mechanisms for the rearrangement¹⁶ are a unimolecular (eq 4) and a bimolecular pathway (eq 5). The former is a retention mechanism involving a rearrangement *via* 9 where the two oxygen atoms in 5 come from the same oxygen molecule. The latter pathway of eq 5 involves six-

(15) Murray, R. W. In *Singlet Oxygen*; Wasserman, H. H.; Murray, R. W., Ed.; Academic Press: New York, 1979; p 93.

(16) Von Itstein, M.; Jenkins, I. D. *J. Chem. Soc., Chem. Commun.* 1983, 164.



membered diperoxide 10 as the dimer of 8, by analogy with the dimer formation from carbonyl oxides,¹⁷ resulting in scrambling of the two oxygen atoms as shown. The results in Table IV clearly support the unimolecular retention rearrangement *via* phosphadioxirane intermediates (eq 4).¹⁸ The rearrangement was shown to be competitive with the trapping by Ph₃P since the yield of rearranged product was lowered by the presence of higher phosphine concentrations (cf. runs 8, 12, and 13 in Table III).

Another evidence for phosphadioxiranes is the results of theoretical calculations. Repeated *ab initio* calculations (RHF/STO-3G*¹⁹ and RHF/3-21G*²⁰) failed to yield a stable dipolar structure for 8 (R = HO).²¹ This means that the 1,3-dipolar species cannot be an intermediate on the basis of the theoretical calculations. On the other hand, phosphadioxirane 7 (R = HO) was shown to possess an energy minimum. The resulting structure is a stable phosphorane structure where one of peroxidic oxygen atom is situated in an apical position. The resulting cyclic form 11 shown in Figure 2 is of trigonal bipyramidal structure and its quasiapical bonds are, as usually observed for five-coordinated phosphoranes,²² longer than those of equatorial ones. Thus, the theoretical calculations predict phosphadioxiranes as the only one possible intermediate.

Houk and Foote et al.^{23,24} have obtained similar results for parent phosphadioxirane (2, R = H). They have calculated the formation mechanism and structural details of parent phosphadioxirane by detailed higher level calculations.

Comparison of XOO Species. The present results, both trapping and theoretical, for R₃POO species are quite contrasted to the reported cases of carbonyl and related oxides. In carbonyl oxides, their dipolar structure (1a, X = R₂C) is stable because of the high double bond nature of the C–O bond, causing a high activation energy for the cyclization to dioxiranes.² This is a reason for no obser-

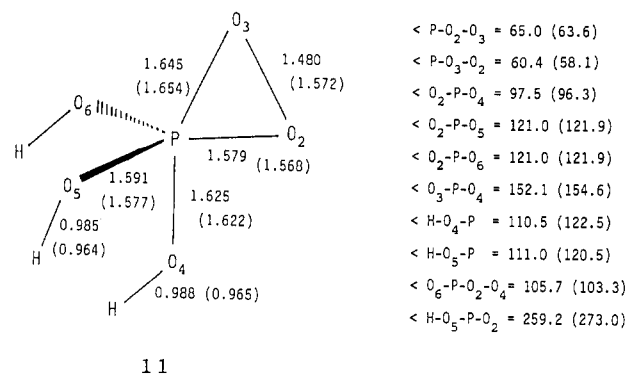
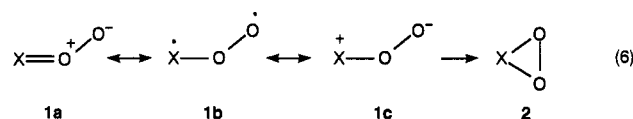


Figure 2. Optimized geometries of trihydroxyphosphadioxirane (11) by RHF/STO-3G* and RHF/3-21G*(*), total energies being -708.07843 and -713.10466 au, respectively. Values in angstroms and degrees; results by 3-21G* are shown in parentheses.

vation of thermal isomerization of carbonyl oxides 1a to dioxiranes 2, which is about 30 kcal/mol more stable than 1a.^{1,2} The situation is almost the same for the case of simple persulfoxides (1, X = R₂S) where the isomerization from 1 to 2 has not been substantiated;^{8b,25} the double bond nature of S–O bonds is significant for persulfoxides.²⁷ In contrast, structure 1a and 1b are shown not to be important for the present case of X = R₃P.



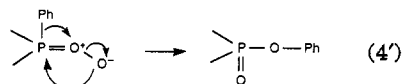
What is the origin for the difference between X = P and C or S? The most important factor seems to be the difference in electronegativities. The electronegativity (EN) difference between oxygen atom (EN = 3.5) and X is 1.0 for X = C and S and as large as 1.4 for X = P. It is expected that the double bond nature of X–O bonds decreases with increasing difference in their electronegativity and hence the contribution of structure 1c will become important for the case of X = P. The cyclization of 1c to form dioxirane 2 is probably facile because of the single bond nature of P–O bond and the attractive neutralization of the plus and minus charges. This might lead to no existence of calculated dipolar structure for R₃POO. The case of nitroso oxides (X = RN) is of another typical one where the electronegativity difference is only 0.4 and hence diradical structure 1b is most important;⁹ the observed cyclization of 1b to 2 for X = RN was explained by the decreased double bond nature in the N–O bond.

These considerations suggest that the 1,3-dipolar structures for 1 are stable only when the electronegativity differences are intermediate (e.g., X = C and S), and otherwise the cyclization to dioxiranes 2 becomes facile.

Conclusion. The peroxidic intermediates in the reaction of trivalent phosphorus compounds with singlet oxygen react as an electrophilic O-atom transferring agent, not exhibiting nucleophilic or radical reactivities. Involvement of phosphadioxirane intermediates is suggested on the basis of relative reactivity of added substrates, the

(17) Bartlett, P. D.; Traylor, T. G. *J. Am. Chem. Soc.* **1962**, *84*, 3408.

(18) A third mechanism is suggested as the unimolecular conversion of the dipolar form 8 to phosphinate 5. This mechanism could explain the retention of doubly-labeled ¹⁸O atoms, but any picture leading to the phosphinate always involves a cyclization of outer oxygen atom to P



(see eq 4'). That is, the difference between eqs 4 and 4' is only the timing of cyclization. Hence, the rationalization by eq 4 is more straightforward and in line with the intermolecular trapping experiments.

(19) RHF/STO-3G*: Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1976**, *64*, 5142.

(20) RHF/3-21G*(*): Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.

(21) The calculated structures involved an imaginary frequency, suggesting no stable structure for 8.

(22) Smith, D. J. H. Reference 12b, p 1235.

(23) Nahm, K.; Li, Y.; Evanseck, J. D.; Houk, K. N.; Foote, C. S. *J. Am. Chem. Soc.*, in press.

(24) We acknowledge Professor Foote for generously sending the preprint.

(25) In cases of cyclic dithianes, the isomerization from 1 to 2 has been suggested by trapping experiments.²⁶

(26) (a) Sheu, C.; Foote, C. S.; Gu, C.-L. *J. Am. Chem. Soc.* **1992**, *114*, 3015. (b) Clennan, E. L.; Wang, D.-X.; Yang, K.; Hodgson, D. L.; Oki, A. R. *J. Am. Chem. Soc.* **1992**, *114*, 3021.

(27) Jensen, F.; Foote, C. S. *J. Am. Chem. Soc.* **1988**, *110*, 2368.

^{18}O -tracer study for rearranged phosphinate, and also by theoretical calculations.

Experimental Section

GC/MS spectra were recorded with a JEOL D300 mass spectrometer. GLC analyses were performed with a Yanagimoto G180 gas chromatograph with 1- or 2-m columns: PEG 20M, 20% on Chromosorb WAW; Carbowax 300M, 20% on Chromosorb WAW; Ultrabond PEG.

Materials. Tributyl phosphite (**3**) and solvents were distilled before use. Substituted diphenyl sulfoxides were described previously.⁵ $^{18}\text{O}_2$ (99% pure) gas from CEA was diluted with natural oxygen gas. Other reagents were of commercial sources and used without further purification.

Typical Procedure of the Photooxidation. A 2-mL acetonitrile solution of 10 mM tributyl phosphite (**3**), 0.1 M diphenyl sulfoxide, and 0.1 mM Methylene Blue (MB) in a 10-mL Pyrex test tube with a septum rubber cap was purged with oxygen for 2 min and irradiated at 20 ± 2 °C for 1 h with a 300-W medium pressure Hg lamp through a 5% NaNO_2 filter solution (i.e., ≥ 400 nm). The formation of tributyl phosphate and diphenyl sulfone was determined by GLC with use of a 1-m column of PEG 20M at 60–250 °C. The products were identified by GC/MS in comparison to authentic samples. Control experiments showed that Ph_2S and Ph_2SO were not oxidized in the absence of phosphite **3** under the same conditions.

The relative rates for the oxidation of diphenyl sulfoxides and sulfides during the photooxidation of **3** were determined from the relative product yields in the presence of 50 mM each of diphenyl sulfoxide and the other substrate, and listed in Table II. The conversions of added substrates were below 2%.

The photooxidation of triphenylphosphine (**4**) was carried out similarly; contaminant triphenylphosphine oxide in **4** was less than 1%. The conversion of added substrates was less effective in comparison to the above case of **3**. The formation of rearranged phenyl diphenylphosphinate (**5**) was ascertained by GC/MS in comparison to the authentic sample. The results are listed in Tables II and III.

^{18}O -Tracer Study. A 2-mL solution of 20 mM Ph_3P and 0.1 mM MB was placed in a 5-mL test tube with a septum rubber cap. After the solution was purged with argon, oxygen gas ($^{32}\text{O}_2/^{34}\text{O}_2/^{36}\text{O}_2 = 100:0.5:6.2$) was introduced into the test tube through a syringe by exhausting the argon gas with another syringe. After irradiation for 1 h at ≥ 400 nm, the rearranged product, phenyl diphenylphosphinate (**5**), was analyzed by GC/MS with a 1-m GC column of Ultrabond PEGS.

The data in Table IV summarizes the mass spectral data of **5** obtained by two determinations. The observed $M/(M+2)/(M+4)$ ratio for **5** ($M = 294$) using the $^{18}\text{O}_2$ gas was 100:11.8:5.9, the $M+4$ value of which is in contrast with the value with natural oxygen gas (i.e., 100:10.5:0.3). The net difference by using the $^{18}\text{O}_2$ gas is then 100:1.3:5.6.

The theoretical values for the retention and scramble pathways using the $^{18}\text{O}_2/\text{O}_2$ gas were calculated according to eqs 4 and 5, respectively, and are listed in Table IV.

Theoretical Calculations. The calculations were carried out on HITAC M-680H and S-820/80 computers using a GAUSSIAN 82 program system.²⁸ The basis set consisted of STO-3G*¹⁹ and 3-21G(*).²⁰ The structures were optimized with the restricted HF (RHF) procedure by use of standard gradient techniques. No stable structure was calculated for dipolar phosphite peroxide (**8**, $\text{R} = \text{HO}$). The only one calculated stable structure was phosphadioxirane **11** of a phosphorane structure as shown in Figure 2. The total calculated energies of **11** were -708.07843 and -713.10466 au by RHF/STO-3G* and RHF/3-21G(*), respectively.

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(28) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. *GAUSSIAN 82*; Carnegie-Mellon University: Pittsburgh, PA, 1982.