Triplet-Sensitized Photorearrangements of 2-Phenylallyl Phosphites

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Abstract: The triplet-sensitized photorearrangements of 2-phenylallyl phosphites **1**, **3**, and **4** to the corresponding 2-phenylallylphosphonates **1a**, **3a**, and **4a** are shown to proceed with complete regioselectivity (**5** → **6** and Scheme 1). A mechanism is proposed in which the 1,2-biradical-like styryl triplet, **9**, adds oxidatively to three-coordinate phosphorus to generate a cyclic, triplet, phosphoranyl *1,3-biradical*, **10**, that undergoes rapid subsequent β scission to generate product 2−phenylallylphosphonate, **11**. Phosphonate **1a** is formed near-quantitatively from dimethyl 2-phenylallyl phosphite, **1**. Phosphites **2**−**4**, with phosphorus contained in a five-, six-, or seven-membered ring, respectively, photorearrange much more slowly, although yields of phosphonates **3a** and **4a** of 50−70% are generated. Quantum yields for the formation of phosphonates **1a**, **3a**, and **4a**, on sensitization by triplet triphenylene, were determined to be 0.25, 0.003, and 0.005, respectively, in benzene. Similar values were found in acetonitrile and benzene using benzophenone as triplet sensitizer. Rate constants, k_q, for efficient quenching of the triplets of benzophenone (phosphorescence quenching) and triphenylene (photothermal lense measurements) were all in the range $4.0{-}5.4 \times 10^9$ M^{-1} s^{-1}. The low quantum yields for phosphonate formation from **3** and **4** (and presumably **2**), therefore, result from the relative inefficiencies of reactions of their 2-phenylallyl triplets toward phosphorus. This is ascribed to the large reduction in the rate of isomerization of the kinetically formed initial 1,3-biradical, **23**, to the thermodynamically more stable species, **24**, an effect found in spiro phosphoranyl monoradicals. A reduction in the rate of β scission of biradical **23**, caused by its spiro structure, also may play a role. The failure of the 3-phenylallyl phosphite **7** to undergo the same cyclic photorearrangement as **1** is ascribed to the inability of the benzyl radical-like terminus of triplet **7** to react with phosphorus. Phosphite homolog **8** also is inert toward cyclic photorearrangement via a six-membered ring 1,3-biradical (**28**) analogous to **10**. The reactivity patterns of phosphites **1-4**, **7**, and **8** can be rationalized in terms of the 1,2-biradical nature of the triplet styryl moiety and factors known to govern the formation and permutational properties of phosphoranyl *mono*radicals.

Introduction

Aryl-substituted alkenes in the first triplet excited state have been intensely studied of late.[1] The Caldwell group has shown them to be accurately characterized as orthogonal 1,2-biradicals.[1e,k,l] As such they behave like alkyl mono free radicals and can undergo ring-opening reactions[1e] and, along with other triplet alkenes, add to alkenes[2] and abstract hydrogen from carbon−hydrogen bonds.[2,3] Of particular relevance to the present research are hydrogen abstractions by triplet arylalkenes that occur in *intramolecular* fashion.[3]

The known reversible addition of primary alkyl radicals to trialkyl phosphites to form phosphoranyl radicals, e.g. **16** (eq 5),[4] suggested to us the possible intramolecular trapping of a triplet alkene moiety by three-coordinate phosphorus to give a phosphoranyl 1,3-biradical (e.g. **10**, Scheme 1). Indeed we reported preliminary investigations of 2-phenylallyl phosphites whose triplet-sensitized photorearrangements are consistent with this model.[5a,b] The present paper records mechanistic studies directed at understanding the surprising *inefficiency* of these

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Table 1. Yields of Triplet-Sensitized Photorearrangements of 0.1−0.5 M Deoxygenated Solutions of **1**, **3**, and **4** in Pyrex at 350 nm

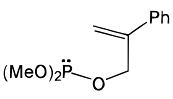
phosphite	sens[b]	% conv	% yield[a] NMR/GC	% yield[a] isolated	solvent
1	T[c]	100	97[g]	86	C_6H_6
1	B[d]	100	95[h]	*i*	C_6H_6
3	T[c]	72	57[g]	54	C_6H_6
3	P[e]	34	33[h]	*i*	C_6H_6
4	T[c]	83	68[g]	59	C_6H_6
4	B[f]	39	71[h]	*i*	CH_3CN
4	P[f]	42	69[h]	*i*	CH_3CN

[a] Based on phosphite consumed. [b] B, benzophenone; P, *p*-methoxyacetophenone; T, triphenylene. [c] 0.5 M in phosphite and sensitizer.[d] 0.1 M phosphite, 0.1 M sensitizer. [e] 0.1 M phosphite, 0.2 M sensitizer, 300 nm lamps. [f] 0.1 M phosphite, 0.3 M sensitizer. [g] ^{31}P NMR. [h] GC. [i] Not determined.

photorearrangements when phosphorus is included in a 5-, 6-, or 7-membered ring (**2**−**4**). A rationale for the reported results is offered that is based on knowledge of reactions involving phosphoranyl monoradicals. The reluctance of phosphite analogs **7** and **8** to undergo photoisomerization to phosphonates is likewise explained in terms of principles derived from earlier work on phosphoranyl monoradicals.[5c]

Results

Product Studies. The photorearrangements of 0.01−0.1 M deoxygenated solutions of phosphites **1**−**4** were carried out in cyclohexane, benzene, and acetonitrile. Sensitizers were chosen with triplet energies that should be above that for the 2-phenylallyl functionality of **1**−**4**, assumed to be close to the value for α-methylstyrene (E_T = 61.7,[1k] 62.6[6] kcal/mol): Ph_2CO (E_T = 69.2 kcal/mol[7]), triphenylene (E_T = 67.0 kcal/mol[7]), and *p*-methoxyacetophenone (PMAP) (E_T = 71.7 kcal/mol[7]). Light of appropriate wavelengths was transmitted through Pyrex to ensure that energy was absorbed only by the sensitizer. A benzene solution, 0.1 M in both phosphite **1** and benzophenone sensitizer, irradiated through Pyrex, showed **1** to be totally converted to its phosphonate, **1a**, in 4 h in near-quantitative yield (Table 1). By contrast an initial indication of the remarkable effect of placing phosphorus in a ring was seen when a parallel reaction of phosphite **2** gave <1% of the corresponding phosphonate in 48 h. GLC and/or isolated yields of phosphonate (product accountabilities based on consumed phosphite) from photorearrangement of **1**, **3**, and **4** are recorded in Table 1. Notably, in addition to undergoing photorearrangement slowly, phosphites **3** and **4** with phosphorus in a ring gave reduced yields of phosphonate compared to **1**. A careful look at the sluggish, triplet-sensitized photorearrangement of **3** shows it to be accompanied by the formation of the apparent dimer of the 2-phenylallyl radical, $(PhC{=}CH_2CH_2)_2$ (ca. 0.2%), and α-methylstyrene (ca. 1%). These side products, which may come from P−O homolysis, are not found in the very efficient triplet-sensitized photorearrangement of **1**.



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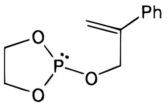

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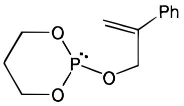

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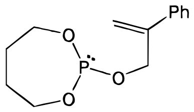

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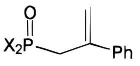


1a-4a

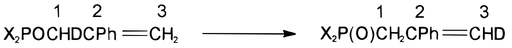
1a, X = MeO; **2a**, X_2 = OCH_2CH_2O; **3a**, X_2 = $OCH_2CH_2CH_2O$; **4a**, X_2 = $OCH_2CH_2CH_2CH_2O$

Table 2. Quantum Yields ϕ_P for Triplet-Sensitized Formation of Phosphonates **1**, **3**, and **4**[a]

phosphite	solvent	ϕ_P[b] B[c]	ϕ_P[b] T[c]
1	CH_3CN	0.32	
	C_6H_6	0.22	0.25
3	CH_3CN	0.004	
	C_6H_6	0.003	0.003
4	CH_3CN	0.005	
	C_6H_6	0.004	0.005

[a] Degassed solutions, 0.05 M sensitizer, 0.01−0.07 M phosphite, 335 nm light. [b] One sigma error of 2−6% from 3−5 determinations at several conversions. [c] B, benzophenone; T, triphenylene.

Regiochemistry. Phosphites **1**, **3**, and **4**, deuterium labeled at C1 as shown in **5a**, **5c**, and **5d**, underwent photorearrangement under triplet sensitized conditions in the regiospecific manner represented by the conversion **5** → **6** (eq 1). The regiochemistry was followed by ^{2}H NMR which showed the product phosphonates (**6**) to have deuterium attached only to the carbon designated C1 in eq 1. E.g., phosphonate **6a** from phosphite **5a** displayed equal-intensity deuterium resonances only at δ 5.28 and 5.43 (C_6H_6)) assigned to the diastereotopic deuteria at C1 (eq 1). This regiochemistry was confirmed for phosphites **5a** and **5c** with PMAP as sensitizer and for **5a**, **5c**, and **5d** with the sensitizers benzophenone and triphenylene. The limits of detection by ^{2}H NMR give a lower limit of regioselectivity of about 95%. In a parallel experiment, deuterium-labeled **1** (**5a**) was directly irradiated through quartz with light from a 450-W medium-pressure lamp. Unlike the sensitized reactions, deuterium was nearly randomly scrambled to give diastereomers **6a** and **15a** in approximately equal amounts. Deuterium at C1 of **15a** was observed at δ 2.65 (**5a** → **6a** + **15a**).



$$\overset{1}{X_2POCHD}\overset{2}{C}Ph{=}\overset{3}{CH_2} \longrightarrow X_2P(O)\overset{1}{CH_2}\overset{2}{C}Ph{=}\overset{3}{CHD} \qquad (1)$$

5a, 5c, 5d **6a, 6c, 6d**

a, X = MeO; **c**, X_2 = $OCH_2CH_2CH_2O$; **d**, X_2 = $OCH_2CH_2CH_2CH_2O$

Quantum Yields. To place the relative reactivities of phosphites **1**, **3**, and **4** on a quantitative basis, the quantum yields (ϕ_P) for formation of phosphonates **1a**, **3a**, and **4a** were determined with the sensitizers (0.05 M) triphenylene and benzophenone which were irradiated with 335-nm light in a Photon Technology Quantacount electronic actinometer. The observed invariance of ϕ_P over a range of phosphite concentrations (0.01−0.07 M) and the measured rate constants of triplet quenching (see below), along with the known triplet lifetimes of the sensitizers,[8] ensured that the triplet energy of the senzitizers was totally transferred to the phosphites. Results are recorded in Table 2. The wide spread in quantum efficiencies confirms the more-qualitative reactivity differences noted for the phosphites.

Triplet Quenching Kinetics. The relative rate constants for triplet quenching, k_q, by phosphites **1**, **3**, **4**, and $(EtO)_3P$ were determined for the sensitizers triphenylene and benzophenone.

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(8) τ_T for benzophenone 50 μs[7] and for triphenylene 55 μs.[7]

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Table 3. Quenching of Triplet States of Triphenylene and Benzophenone

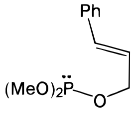
		$10^{-9}k_q$,[a] $M^{-1}\ s^{-1}$	
quencher	solvent	benzophenone[b]	triphenylene[c]
phosphite **1**	CH_3CN	4.0 ± 0.07	4.0 ± 0.2
	C_6H_6		4.4 ± 0.3
phosphite **3**	CH_3CN	4.5 ± 0.08	
	C_6H_6		3.7 ± 0.1
phosphite **4**	CH_3CN	4.1 ± 0.01	
	C_6H_6		5.4 ± 0.4
$(C_2H_5O)_3P$	CH_3CN	1.3 ± 0.04	
	C_6H_6		<0.001
α-methylstyrene	CH_3CN	4.6 ± 0.3	
	C_6H_6	2.7 ± 0.3[d]	3.9

[a] Errors at 1 σ confidence level. [b] From decay of benzophenone phosphorescence. [c] From photothermal lense spectroscopy. [d] Reference 9.

Quenching of the phosphorescence of benzophenone, induced by 325-nm laser excitation, was monitored in acetonitrile and benzene. The quenching kinetics in benzene, however, were not straightforwardly interpretable. Thus, k_q was obtained in acetonitrile only. Since triphenylene is not phosphorescent in solution, k_q was determined by photothermal lense spectroscopy.[10] The k_q values (Table 3) in both types of experiments were determined from observed pseudo-first-order rate constants via the Stern−Volmer approach (see Experimental Section).

Thermal Rearrangement. Numerous control reactions demonstrated the thermal stabilities of phosphites **1**, **3**, and **4** at ambient temperature. However, at 165−170 °C a 1.6 M *p*-cymene solution of **5a** was at least 60% consumed in 24 h to give phosphonate exclusively deuterium labeled at C3, **6a**, along with lesser amounts of a second phosphonate, $MeP(O)(OMe)_2$ (identified by GC), in 3/2 to 5/4 ratios. An approximately 18% yield (based on phosphite consumed) of **6a** were isolated by flash chromatography. Neither reaction nor isolation procedures for **6a** was optimized.

Isomers and Homologs of 1. Placement of the phenyl group at C3 of the allyl functionality (phosphite **7**) rendered that molecule inert to photorearrangement under benzophenone sensitization. Cis−trans isomerization about the double bond, however, was observed. Homologation of the allyl (2-propenyl) chain gave a molecule (phosphite **8**) that yielded a variety of unidentified products on benzophenone-sensitized reaction.



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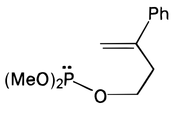

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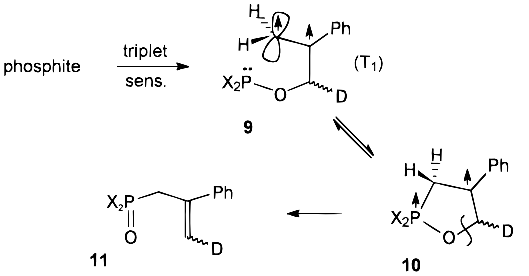
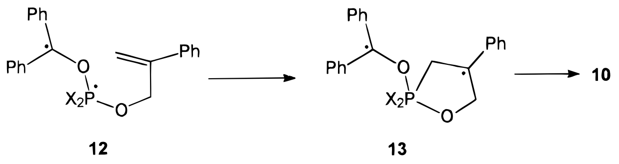
Discussion

2-Phenylallyl Phosphites. The observed efficient triplet quenchings and specific regiochemistries of the reactions of phosphites **1**, **3**, and **4** are consistent with the formation of the triplet styryl unit (**9**) with the unpaired electrons in adjacent orthogonal orbitals. This moiety adds oxidatively to phosphorus to generate a phosphoranyl 1,3-biradical (**10**, Scheme 1). Subsequent intersystem crossing and β scission (**10** → **11**) to form P=O and C=C π bonds yields the 2−phenylallylphosphonate (**11**). Chemically, this transformation amounts to an intramolecular Arbuzov rearrangement. $\Delta H°$ for transformation of trimethyl phosphite ($(MeO)_3P$) to its phosphonate ($MeP(O)(OMe)_2$) has been measured to be exothermic by 24 kcal/mol.[1k] The benzylic nature of the carbon radical center may stabilize **10** and facilitate the photorearrangement.

Scheme 1



Triplet ketones are known to add oxidatively to three-coordinate phosphorus,[12] and the phosphorescence of benzophenone was quenched by $(EtO)_3P$ (Table 3). The quenching of benzophenone phosphorescence by phosphites **1**, **3**, and **4**, therefore, might be chemical in nature. Readily envisaged is a process for the observed photoisomerizations whereby adduct **12**, formed by oxidative addition of triplet benzophenone to phosphorus, cycloadds to the styryl moiety to form **13**. (The trapping of phosphoranyl monoradicals by alkenes is a known reaction.[13]) Elimination of benzophenone from **13** generates 1,3-biradical **10**. The possibility that the observed photorearrangements are initiated by single electron transfer from the styryl phosphites to triplet benzophenone is ruled out by our recent study of the rearrangements of **1**, **3**, and **4** induced by electron transfer to the first singlet excited state of 9,10-dicyanoanthracene (DCA) in acetonitrile.[14] Though the same phosphite → phosphonate rearrangement is induced by singlet DCA, those processes are characterized by low and nearly identical quantum yields for phosphonate formation from **1** ($\phi_P = 0.03$) and **3** ($\phi_P = 0.02$)[14] and are clearly different mechanistically from the reactions discussed in the present paper.



Triphenylene is an ideal triplet sensitizer for the photorearrangements of **1**, **3**, and **4** as it does not possess a carbonyl functionality; and the energy of its first excited singlet state (83.4 kcal/mol[7]) is much too low for it to be a singlet sensitizer (E_S for α-methylstyrene is 99.6 kcal/mol[6]). Moreover, the free energy change for electron transfer to triplet triphenylene in benzene is unfavorable by 44 kcal/mol.[15] Hence triphenylene can only transfer triplet energy to phosphites **1**, **3**, and **4** (triplet energy, E_T, for triphenylene = 66.5 kcal/mol[7]; E_T for α-meth-

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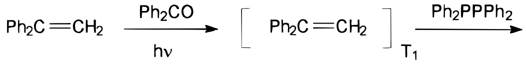
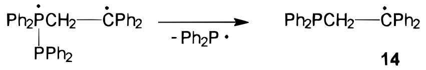
ylstyrene = 62 kcal/mol[1k,6]). Moreover, PMAP, whose $\pi-\pi^*$ triplet is generally less chemically reactive[16] than the $n\rightarrow\pi^*$ triplet of benzophenone, effectively sensitizes these photorearrangements (Tables 1 and 2). The similarities of the k_q and ϕ_P values for benzophenone and triphenylene sensitizations suggest strongly that *both* act as triplet sensitizers. Evidently triplet energy transfer from benzophenone to the styryl moiety of these phosphites is faster than any chemical quenching process. Lacking a triplet acceptor, (EtO)$_3$P is unable to quench triplet triphenylene. Its 3-fold reduction in k_q with benzophenone, compared to the values for phosphites **1**, **2**, **3**, and **4**, is consistent with its quenching of benzophenone phosphorescence by a chemical mechanism.

The triplet-sensitized photorearrangements of the above phosphites find some *intermolecular* analogies,[12,17] the most direct being the xanthone-sensitized reaction of 1,1-diphenylethene with tetraphenyldiphosphine (eqs 2−4).[17] Attack at phosphorus by the terminal carbon of the excited alkene was proposed to lead to displacement (eq 3), perhaps via a phosphoranyl 1,3-biradical. Alkoxy-radical-like reactions of benzophenone triplets[12d] with tetraphenyldiphosphine[12c] and (EtO)$_2$POP(OEt)$_2$12d have been reported. Photoreactions of other aromatic ketones,[12d] 4,4′-dimethoxybenzothioketone,[12f] and quinones[12d] with (EtO)$_2$POP(OEt)$_2$ and/or tetraethyldiphosphine likewise illustrate the 1,2-biradical-like reactivity of triplet functionality toward three-coordinate phosphorus. Moreover, aroylmethyl and acylmethyl dimethyl phosphites, RCOCH$_2$OP(OMe)$_2$, undergo photorearrangement to CH$_2$=CRP(O)(OMe)$_2$, perhaps via a triplet 1,3-biradical intermediate similar to **10**.[12e]



$$\mathrm{Ph_2C{=}CH_2} \xrightarrow[h\nu]{\mathrm{Ph_2CO}} \left[\mathrm{Ph_2C{=}CH_2}\right]_{T_1} \xrightarrow{\mathrm{Ph_2PPPh_2}} \qquad (2)$$



$$\mathrm{Ph_2\dot{P}(PPh_2)CH_2{-}\dot{C}Ph_2} \xrightarrow[-\,\mathrm{Ph_2P}\cdot]{} \mathrm{Ph_2PCH_2{-}\dot{C}Ph_2} \qquad (3)$$

14

$$\xrightarrow{\mathrm{Ph_2P}\cdot} \mathrm{Ph_2C{=}CHPPh_2} + \mathrm{Ph_2PH} \qquad (4)$$

Singlet Processes. The observed thermal rearrangement of **1**, in contrast to its room-temperature triplet-sensitized photorearrangement, occurs only at relatively high temperatures. Its regiochemistry and the temperature required are consistent with earlier results for other allyl phosphites.[18] Side product MeP(O)(OMe)$_2$ is the obvious result of an *intermolecular* thermal Arbuzov process involving two molecules of **1**. Whether this formally 2,3-sigmatropic process (based on its regiochemistry, **5a** → **6a**) occurs via a concerted or stepwise mechanism is unknown. Conceivably, triplet phosphoranyl biradical **10** may be converted by intersystem crossing to the same ground state singlet cyclic biradical formed in a stepwise, thermal rearrangement that is then rapidly and irreversibly converted to **11**.

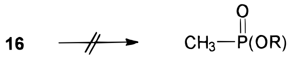
By contrast, direct photoirradiation of **5a** (Results Section), **5c**, and **5d** yields both phosphonate regioisomers (e.g. **6a** and **15a** from **5a**) *in nearly equal amounts*.[19] Control experiments show that this scramble of label does not occur at the phosphite or phosphonate stage (Experimental Section) but is intrinsic to the photorearrangement process.[19] Two possible mechanisms are the following: (1) competing, concerted 1,2- and 2,3-sigmatropic rearrangements; and (2) scission to a caged phosphonyl/2-phenylallyl radical pair that bonds randomly to phosphorus at C1 and C3. These studies will be reported separately.[19] They are relevant to the present study in that they show that the styryl-like *singlet excited states* of **1**, **3**, and **4** do not undergo rapid intersystem crossing to the triplet (**9**) prior to reaction, which would have led to the regiospecific process observed on triplet sensitization.

Effects of Ring Size on Φ_P. The greatly reduced quantum efficiencies encountered when phosphorus is included in a 6- or 7-membered ring (phosphites **3** and **4**) could arise from inefficient triplet energy transfer or because the styryl-like triplet excited state is relatively unreactive. The essentially equal, near diffusion-controlled k_q values measured for phosphites **1**, **3**, and **4** (Table 3) show triplet quenching to be very rapid in all cases and comparable to that measured for α-methylstyrene itself (Table 3). Indeed at the concentrations of phosphites used, triplet energy transfer, in competition with triplet−singlet decay, should be 100% efficient.[20] Evidently, based on the ϕ_P values of Table 2, triplet **1** undergoes cyclization and formation of product phosphonate relatively efficiently, while for triplet **3** and **4** these steps are inefficient.

A reasonable understanding of the inefficiencies of the photorearrangements of **3** and **4** can be obtained by consideration of known features of phosphoranyl *monoradicals*: the reversibility of the addition of alkyl radicals to trialkyl phosphites and the retardation of the rates of apical−equatorial exchange of phosphorus substituents when phosphorus is part of a spiro ring system. The reversibility of the addition of methyl radical to a series of trialkyl phosphites (eqs 5 and 6) has been demonstrated by ESR techniques that showed the signal intensity for **16**, monitored under conditions of steady-state methyl radical flux, to be strongly temperature dependent.[4a] Furthermore, alkyl radical from β scission could not be observed, suggesting that this cleavage is too slow to compete with α scission to regenerate P(OR)$_3$. This was confirmed by chemical studies[4b] that demonstrated that no stable products result from the room temperature reaction of ethyl radical with (MeO)$_3$P or (EtO)$_3$P. By contrast, ethyl radicals react with PhCH$_2$OP(OMe)$_2$ to give C$_2$H$_5$P(O)(OMe)$_2$ and bibenzyl, presumably by way of **17**.[4b] The formation of the relatively stable benzyl radical by β scission is a comparatively rapid process that effectively traps **17** in competition with reformation of ethyl radical (α scission).

$$\mathrm{CH_3}\cdot + \mathrm{P(OR)_3} \rightleftharpoons \mathrm{CH_3{-}\dot{P}(OR)_3} \qquad (5)$$

16



$$\mathbf{16} \not\longrightarrow \mathrm{CH_3{-}P(O)(OR)_2} + \mathrm{R}\cdot \qquad (6)$$

$$\mathrm{X_2P(O)\overset{1}{C}HD\overset{2}{C}Ph{=}\overset{3}{C}H_2} \qquad \mathrm{C_2H_5{-}\dot{P}(OMe)_2(OCH_2Ph)}$$

15a, 15c, 15d **17**

a, X = MeO; **c**, X$_2$ = OCH$_2$CH$_2$CH$_2$O;
d, X$_2$ = OCH$_2$CH$_2$CH$_2$CH$_2$O

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[15] (a) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. (b) Calculations made using for triphenylene E_S = 3.62 eV,[7] E_{red} = −2.22 eV vs SCE, CH$_3$CN (Julliard, M.; Chanon, M. *Chem. Br.* **1082**, *18*, 558); for (EtO)$_3$P E_{ox} = 1.57 eV vs SCE, CH$_3$CN (Ohmori, H.; Nakai, S.; Masui, M. *J. Chem. Soc., Perkin Trans 1* **1979**, 7023); and α-methylstyrene E_{ox} = 1.76 eV vs SCE, CH$_3$CN (Katz, M.; Riemenschneider, P.; Wendt, H. *Electrochem. Acta* **1972**, *17*, 1595).

[16] Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings Pub.: Menlo Park, CA, 1978; Chapter 10.

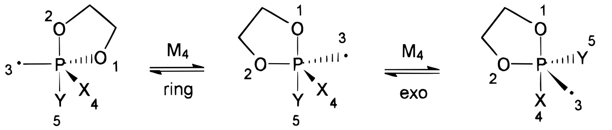
[17] Okazaki, R.; Hirabyashi, Y.; Tamura, K.; Inamoto, N. *J. Chem. Soc., Perkin Trans 1* **1976**, 1034.

[18] Herriott, A. W.; Mislow, K. *Tetrahedron Lett.* **1968**, 3013.

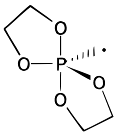
[19] Lee, S.-G.; Baik W.; Wu, Y.-W.; Tabet, M. Unpublished results from this laboratory.

[20] This can be seen by consideration of the measured values of k_q of Table 3 of 10^9−10^{10} M^{-1} s^{-1}, the triplet lifetimes for benzophenone (50 μs[8]) and triphenylene (55 μs[8]), and the concentration range of phosphites employed (0.01−0.07 M).

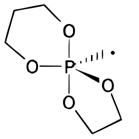
Kinetic ESR work[6] has established that the most rapid permutation available to the near-trigonal bipyramidal phosphoranyl radical represented by **18** is an exchange involving the two exocylic substituents (X and Y) and the position occupied by the odd electron (**18** $\rightleftharpoons$ **19**). This exchange is of mode 4 (M_4).[21] Because it involves ligands not included in the ring, it is termed M_4(exo). It occurs rapidly even at 200 K with substituent-dependent rate constants (k_{exo}) of 10^7-10^9 s^{-1}.[22] At higher temperatures an M_4(ring) permutation participates (**18** → **20**) that includes the ring atoms. At 273 K k_{ring} is about 10^6-10^8 s^{-1}. Strikingly, the spiro radical **21** could not be induced to undergo rapid exchange even at 393 K.[23]



20 **18** **19**

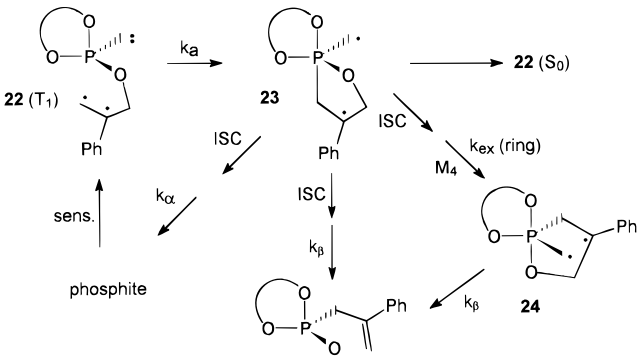


21



26

Scheme 2



Scheme 2 depicts the intramolecular reaction of the styryl triplet of **22** with phosphorus. The new carbon phosphorus bond in the trigonal bipyramidal 1,3-biradical is formed apically, consistent with the implications of kinetic studies of the reverse process, α-scission of carbon–phosphorus bonds of phosphoranyl monoradicals.[24] (The near-trigonal bipyramidal nature of closely related phosphoranyl monoradicals possessing alkyl and oxy substituents is well-established.[25]) If the lifetime of the triplet styryl moiety of these phosphites is similar to that of styrene itself (22–25 ns[1k,m,n,o]) and β-methylstyrene (26,[1k] 27,[1o] 46[1m] ns), then to compete with decay of the triplet, **22** → **23** *must occur with a rate constant* (k_a) *of* 10^7-10^8 s^{-1}. It is proposed that when a spiro system is not involved (i.e. a radical analogous to **18** is present), k_{ex}(ring) of Scheme 2 is *rapid* and *traps kinetically formed* **23** by its conversion to **24**, a lower-energy form. (In **24** ring P–O and P–C bonds are in apical and equatorial positions, respectively, where they are known to be favored *thermodynamically*.[6c,25]) Assuming that **22** → **23** is reversible, as is known for the addition of primary alkyl radicals,[4] then k_α (**23**→**24**) must be of the order 10^7-10^8 s^{-1}. This value is not unreasonable considering the range noted above for k_{ring} for species such as **18** (**18** → **20**). With the spiro system depicted in Scheme 2, *rate-determining* k_{exo}*(ring)* should be much decreased. Therefore, **23** will largely revert to reactant phosphite rather than undergo relatively slow isomerization to **24**. This leads to an *inefficient* conversion of phosphite to phosphonate.

The role of the spiro ring system in suppressing the rate of permutation of substituents is not well understood but almost certainly is related to geometric constraints imposed by the ring on the transition state for exchange. Proposed geometries for the transition state or intermediates for permutational exchange of ligands attached to phosphorus in phosphoranyl monoradicals include the following: local C_{3v} σ^*; trigonal bipyramidal with odd-electron apical; and square pyramidal with odd electron basal.[26] Less sterically constrained rings might allow for rapid permutation to occur. The effect on ϕ_P of a seven- rather than six-membered ring (phosphites **3** vs **4**, Table 2), however, is marginal at best.

In Scheme 2 triplet–singlet intersystem crossing (ISC) of the initial 1,3-biradical **23** precedes its isomerization, its β scission to **25**, and its α scission to ground state phosphite. (Thus, α-scission of **23** in Scheme 2 yields ground state phosphite rather than its triplet (**22**).) However, whether this should be true for all processes available to **23** is not certain. Chemical processes generally compete with ISC of long-lived triplet biradicals.[27] Indeed, 1,3-biradicals in all-carbon 5-membered rings (the cyclopentane-1,3-diyl system) often have *triplet ground states* with lifetimes with respect to ISC of 10–100 ns or greater.[27,28] In phosphoranyl 1,3-biradicals such as **10** or **23**, the phosphorus atom may act to enhance the ease of intersystem crossing and/or perturb the singlet–triplet energy levels. From the rate constants given above for M_4(ring), lifetimes with respect to exchange of the order 1–100 μs are predicted for non-spiro phosphoranyl 1,3-biradicals analogous to **18** (e.g. **10** with X = MeO), long enough to allow ISC to occur before permutation of the sort illustrated by **18** → **19**. The estimate made above for k_α for **23** (10^7-10^8 s^{-1}) would give it a lifetime towards α scission of 10–100 ns, during which ISC may occur leading to α scission to ground state phosphite rather than **22**.

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(21) The modes of permutation of a molecule containing five-coordinate phosphorus have been defined (Musher, J. I. *J. Chem. Ed.* **1974**, *51*, 94. Musher, J. I. *J. Am. Chem. Soc.* **1972**, *94*, 5662). Mode refers to the position of substituents on the trigonal bipyramidal framework before and after the permutation that exchanges their positions without regard to pathway (mechanism). For phosphoranyl radicals the odd electron or vacant position is considered stereochemically to be a fifth ligand. In the mode 4(exo) permutation two ligands that are not part of the ring, along with the odd electron, change positions. Recent calculations have indicated that the permutational possibilities and pathways for phosphoranyl radicals without ligands attached to the phosphorus part of a ring system may be more extensive than for those determined experimentally for **18** and sensitive to the nature of the ligands.[25b]

(22) Cooper, J. W.; Parrot, M. J.; Roberts, B. P. *J. Chem. Soc., Perkin Trans 2* **1977**, 730.

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

(24) Cooper, J. W.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2*, **1976**, 808.

(25) (a) See ref 5c for experimental evidences. Also, Schipper, P.; Jansen, E. H. J. M.; Buck, H. M. *Top. Phosphorus Chem.* **1977**, *9*, 407. (b) For a recent theoretical paper on the relative energies of TBP structures for [MeP(OMe)$_3$]$^\bullet$ and (MeO)$_4$P$^\bullet$, including those with the odd electron either equatorial or apical, see: Gustafson, S. M.; Cramer, C. J. *J. Phys. Chem.* **1995**, *99*, 2267.

(26) See ref 25b and citations therein.

(27) For recent reviews of biradicals, see: (a) Johnston, L. J. *Chem. Rev.* **1993**, *93*. 251. (b) Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24*, 94. (c) Adam, W.; Grabowski, S.; Wilson, R. M. *Acc. Chem. Res.* **1990**, *23*, 165. (d) Caldwell, R. A. In *Kinetics and Spectroscopy of Carbenes and Biradicals*, Platz, M. S., Ed.; Plenum Publ. Co.: New York, 1990; pp 77–116. (e) Johnston, L. J.; Scaiano, J. C. *Chem. Rev.*, **1989**, *89*, 521.

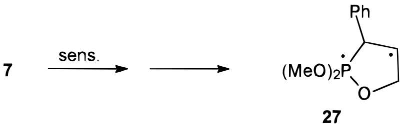
(28) For recent considerations of the effects of structure on the lifetimes of 1,3-cyclopentanediyl triplet biradicals, see: Kita, F.; Nau, W. M.; Adam, W *J. Am. Chem. Soc.* **1995**, *117*, 8670. Engel, P. S.; Lowe, K. L. *Tetrahedron Lett.* **1994**, *35*, 2267.

Scheme 2 might mistakenly be taken to suggest that β scission is *necessarily* more rapid for **24** than for **23**. Indeed, whether there is an apical or equatorial preference for this process in phosphoranyl monoradicals is as yet unclear.[29] In fact in Scheme 2, β scission of **23** may simply not be able to compete effectively with its α scission to phosphite **22**. In fact rapid irreversible trapping of **23** by the rate-determining permutation **23** → **24** would allow β scission of **24** to occur with k_β for **24** less than k_{ex}(ring) for **23** and perhaps even *less* than k_β for **23**.[29] In our view of Scheme 2 outlined above, for the overall photoprocess to be efficient, k_{ex}(ring) for **23** → **24** must be of the same order or greater than that for **23** → phosphite. This would place k_β for **23** → **25** at less than 10^7-10^8 s^{-1}. However, if **23** → **24** is very slow, as in the spiro systems, the product forming β scission for the slow, inefficient production of **25** might even be **23** → **25**.

It is difficult to estimate a priori what k_β for either **23** or **24** should be. These scissions might be extremely rapid since the formation of two π bonds renders the reaction very favorable energetically. Carbon-centered 5-membered-ring triplet 1,3-biradicals, however, do not typically readily undergo such ring openings.[27] Nevertheless, the phosphorus center and the availability of d orbitals set this case apart.

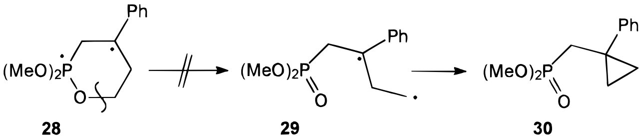
A second potential factor that also should be considered is the known reduction in k_β for phosphoranyl monoradicals on placement of phosphorus in a 5-membered ring. Indeed, the octamethyl ring-substituted analog of **21** gives no evidence for β scission even at 45 °C[13a] and must be generated well above 100 °C for the chemical products of ring-opening to be observed.[30] As noted above, the ESR spectrum for **19** persists at 120 °C.[23] By contrast, $(t\text{-BuO})_4P^\bullet$ and $[t\text{-BuOP(OEt)}_3]^\bullet$ are subject to β scission at −70 °C.[31] In all of the phosphoranyl 1,3-biradicals proposed as intermediates for the photorearrangements of **1**−**4**, it is the same 5-membered ring that must undergo β scission. Indeed, part of the effect of the OCH_2CH_2O attached to phosphorus in **21**, and its tetramethyl-substituted analog, may be to slow the β scission within the 5-membered ring. What the influence of a 6- or 7-membered ring in a phosphoranyl monoradical is on the β scission of the 5-membered ring of a species such as **26**, and by inference on **23** or **24**, is unknown and intrinsically difficult to study. Thus in radicals analogous to **20**, but with phosphorus in a 6- rather than 5-membered ring, only ring-opening β scission occurs to the exclusion of β scission of ethoxy groups also attached to phosphorus (X = Y = ethoxy).[31] For **20** itself for X = Y = ethoxy both ring and ethoxy C−O β scission occur.[31] Radical **26**, therefore, is likely to undergo exclusive scission of the 6-membered ring.

Structural Variations in the Styryl Chromophore. The failure of the attempted triplet-sensitized photo-Arbuzov reaction of **7** is consistent with the potential reactive carbon center being benzylic, a reflection of the 1,2-biradical character of such triplet moieties. Thus, it has been found that benzyl radicals from intermediate **17** fail to react with $PhCH_2OP(OMe)_2$ or at least are not trapped by formation of $PhCH_2P(O)(OMe)_2$.[4b] This is in accord with the relatively stable nature of the benzyl radical and the weakness of the phosphorus−carbon bond to be formed. By analogy, formation of phosphoranyl 1,3-biradical from triplet **7** (**7** → **27**) likely is too unfavorable thermodynamically. The carbon radical center of **27** lacks the stabilizing phenyl substituent found in **10**. Moreover, β scission of any **27** formed,



to generate the 1-phenylallylphosphonate, probably is unable to compete with the α scission reforming phosphite **7**.

Disappointingly, the potential 1,3-biradical **28** from **8**, the homolog of **1**, failed to yield a clean formation of phosphonate product of any kind. Evidently, even if **28** is generated, the β scission shown is not rapid enough to generate 1,3-biradical **29** that might close to cyclopropyl product **30**. Ethoxy phosphoranyl monoradicals $(EtO)_4P^\bullet$ undergo β scission at 25 °C with



k_β of only 3×10^3 s^{-1}.[32] Clearly, this step would be too slow to trap an intermediate (**28**) undergoing α scission to reform phosphite **8** with k_α of the order 10^7-10^8 M^{-1} s^{-1} (see above). Moreover, the formation of **28** involving a 6-membered ring may be kinetically and/or thermodynamically disfavored compared to the formation of 5-membered ring 1,3-biradicals like **10**.

Conclusions

The photorearrangements of 2-phenylallyl phosphites, initiated by triplet sensitization, proceed with essentially complete regioselectivity. The results are consistent with the mechanism of Scheme 1 involving a novel phosphoranyl 1,3-biradical, **10**. The efficient reaction of phosphite **1** and the failure of phosphite **7** to undergo an analogous photorearrangement are understood in terms of the 1,2-biradical model of triplet arylalkenes set forth by Caldwell.[1e,k,m] Thus, reaction of **1** involves attack at phosphorus by what is essentially a primary alkyl radical, a species known to add oxidatively to phosphites. The terminus of triplet **7**, by contrast, resembles a relatively stable benzyl radical, an intermediate characteristically unreactive toward phosphites. The low quantum yields encountered for the photorearrangements of phosphites **3**, **4**, and presumably **2** result not from inefficient transfer of triplet energy but rather because the triplet styryl moiety has a reduced reactivity toward phosphorus. A reasonable understanding of the latter is found by consideration of the known greatly reduced rates of ligand exchange for phosphoranyl monoradicals of spiro structure.[23] It is proposed that the rate-determining trapping of reversibly formed intermediate **23** by conversion to **24**, Scheme 2, is greatly reduced when phosphorus is placed in a 5-, 6-, or 7-membered ring. This leads to predominant reformation of phosphite rather than a rapid **23** → **24** step, followed by β scission to phosphonate **25**. The known reduction in rate of β scission for phosphoranyl monoradicals, when phosphorus is contained in a small-ring spiro system,[13a,30] also may be important. The reactivity trends seen for phosphites **1**−**4**, **7**, and **8** are generally interpretable in terms of previously discovered principles[5] governing the reactions of monoradicals with three-coordinate phosphorus, the permutational properties of phosphoranyl monoradicals, and the assumption that the

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[29] ESR results interpreted as evidence for a preference for β scission from the equatorial position have been put forth. See: Roberts, B. P.; Singh, K *J. Chem. Soc., Perkin Trans. 2* **1980**, 1549.

[30] Akhmetkhanova, F. M.; Rol'nik, L. Z.; Pastushenko, E. V.; Proskurnina, M. V.; Zlot-skii, S. S.; Rakhmankulov, D. L. *J. Gen. Chem. USSR* **1985**, *55*, 1810.

[31] (a) Davies, A. G.; Griller, D.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2224. (b) Davies, A. G.; Griller, D.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1972**, 993.

[32] Calculated from the activation parameters given in ref 31a.

triplet 2-phenylallyl moiety behaves as a 1,2-biradical,[1e,l,n] the methylene terminus of which behaves as a primary monoradical. The formation of phosphoranyl 1,3-biradical **10**(**23**, **24**) is most likely further favored by the benzylic nature of the radical centered on carbon.

Experimental Section

Materials. Ether (Et_2O) and tetrahydrofuran (THF) were purified by distillation under nitrogen from sodium/benzophenone. Benzene (Baker Photrex) was used as received. Acetonitrile was distilled over calcium hydride under nitrogen. Trimethyl phosphite was distilled prior to use. Benzophenone (99% pure) and *p*-methoxyacetophenone (PMAP), both from Aldrich, were used as received. Triphenylene was recrystallized from ethanol. 3-Bromo-2-phenylpropene[33] was prepared in 73% yield in routine manner from phenylallyl alcohol on reaction with phosphorus tribromide. Cyclic methyl phosphites,[34] used in the Arbuzov reactions, were prepared by the exchange reaction of the appropriate phosphoramidite (i.e., *N*,*N*-diethyl-1,3,2-dioxaphosphorinan-2-amine or *N*,*N*-diethyl-1,3,2-dioxaphosphepan-2-amine) with excess methanol. 2,5-Diphenyl-1,5-hexadiene was prepared by the literature method.[35] Unless otherwise noted, distillations were performed using a short-path apparatus without distillation column.

Physical Methods. Melting points were obtained on a Thomas Hoover Capillary Melting Point apparatus, and are uncorrected. Proton (^{1}H), deuterium, (^{2}H), carbon (^{13}C), and phosphorus (^{31}P) NMR spectra were taken on Varian XL-300 and Varian Unity 300 NMR spectrometers. Occasional ^{31}P NMR (32.2 MHz) spectra were obtained on a Varian FT-80 NMR. Chemical shifts (δ) are recorded in parts per million from tetramethylsilane (0.00) with the solvent as internal standard: C_6HD_5 (^{1}H) 7.15, (^{13}C) 128.0; $CHCl_3$ (^{1}H) 7.24, (^{13}C) 77.0; C_6DH_5 (^{2}H) 7.15. ^{31}P NMR spectra were referenced to external 85% phosphoric acid.

GC-EIMS (70 eV) analyses were done on a Hewlett-Packard 5971A mass selective detector utilizing a 5890 Series II gas chromatograph equipped with a 30 m X 0.25 mm HP-5 fused silica capillary column. Other low-resolution EIMS (70 eV) along with HRMS (EI, 70 eV) data were obtained on a Finnegan MAT 95 mass spectrometer. Intensities (parentheses) are percentages of the base peak. The molecular ion is indicated by $[M]^+$. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA, and Galbraith Laboratories, Inc., Knoxville, TN.

Photorearrangement Regiochemistry. Reaction solutions were typically 5.00 mL in volume, prepared under nitrogen atmosphere in a glovebag, and then apportioned between a Pyrex 5 mm NMR tube and one or two 12 mm Pyrex tubes, all fitted with 10/30 joints. After 3 to 4 freeze–pump–thaw degassings (0.01 mmHg), the tubes were flame-sealed. Rearrangement on irradiation through Pyrex in a Rayonet apparatus equipped with 350 nm lamps was monitored by ^{31}P and ^{2}H NMR. Control experiments showed rearrangement did not occur in the absence of UV light and/or appropriate sensitizers. Flash chromatography on silica gel (ethyl acetate) yielded the pure phosphonate product which was characterized by ^{31}P, ^{2}H, ^{13}C, and HRMS and comparison with authentic unlabeled material. Deuterium was attached to C1 of product phosphonate with random stereochemistry resulting in an approximately 50/50 ratio of *E* and *Z* ^{2}H regioisomers, as observed by ^{2}H NMR. The regioselectivity, i.e. formation of 1-^{2}H (**6**) vs 3-^{2}H (**15**) phosphonate regioisomer, was also determined by ^{2}H NMR.

PMAP-Sensitized Irradiation of Dimethyl [1-^{2}H]-2-Phenyl-2-propenyl Phosphite (5a). Two solutions were prepared and divided as described above: (1) a 5.00 mL solution of phosphite **5a** (155 mg, 0.689 mmol, 0.138 M) and *p*-methoxyacetophenone (PMAP) (74 mg, 0.50 mmol, 0.10 M) in benzene (Photrex); (2) a 5.00 mL solution of phosphite **1**-**1*d*** (127 mg, 0.564 mmol, 0.113 M) and *p*-methoxyacetophenone (PMAP) (82 mg, 0.55 mmol, 0.11 M) in acetonitrile. After 18 h of irradiation, all of the starting phosphite was consumed (^{31}P NMR). Only the resonance corresponding to the 2-phenylallylphosphonate was observed in the ^{31}P NMR of the reaction mixtures. ^{2}H NMR analysis of the concentrated, crude reaction mixtures for both solvents showed that the rearrangement occurred with complete regioselectivity. Flash chromatography gave only the phosphonate regioisomer, **5a**. ^{31}P NMR (121.4 MHz, C_6D_6) δ 29.10; ^{2}H NMR (46.0 MHz, C_6H_6) δ 5.43 (s, br, 0.5 ^{2}H, $C{=}CH^{2}\mathit{H}$), 5.28 (s, br, 0.5 ^{2}H, $C{=}CH^{2}\mathit{H}$) (50:50 mixture of *E* and *Z* isomers); ^{1}H NMR (299.9 MHz, C_6D_6) δ 2.85 (d, 2 H, $PC\mathit{H}_2$, $^{2}J_{HP} = 22.2$ Hz), 3.29 (d, 6 H, $OC\mathit{H}_3$, $^{3}J_{HP} = 10.8$ Hz), 5.25 (dt, 0.5 H, $C{=}C\mathit{H}^{2}H$, $^{4}J_{HP} = 5.5$ Hz, $^{4}J_{HH} = 0.9$ Hz), 5.38 (d, 0.5 H, $C{=}C\mathit{H}^{2}H$, $^{4}J_{HP} = 5.4$ Hz), 7.01–7.16 (m, 3 H), 7.36–7.44 (m, 2 H). ^{13}C NMR (75.4 MHz, C_6D_6) δ 32.57 (d, $P\mathit{C}H_2$, $^{1}J_{CP} = 138.7$ Hz), 52.17 (d, $O\mathit{C}H_3$, $^{2}J_{CP} = 6.6$ Hz), 116.71 (td, $C{=}\mathit{C}H^{2}H$, $^{1}J_{CD} = 24.2$ Hz, $^{3}J_{CP} = 10.9$ Hz), 126.63, 127.86, 128.50, 139.19 (d, *ipso*-Ph, $^{3}J_{CP} = 10.1$ Hz), 141.17 (d, $\mathit{C}{=}CH^{2}H$, $^{2}J_{CP} = 4.2$ Hz); GC-EIMS (EI −70 eV) *m*/*z* (relative intensity) 227 $[M]^+$ (71), 226 $[M - 1]^+$ (12), 212 $[M - CH_3]^+$ (6), 132 (82), 131 (89), 130 (42), 119 (40), 118 (30), 117 (30), 116 (100), 115 (35), 109 $[(MeO)_2PO]^+$ (55), 95 (27), 94 (25), 92 (41), 91 (23), 79 (45), 77 $[Ph]^+$ (15). $C_{11}H_{14}{}^{2}HO_3P$ $[M]^+$: HRMS $[M]^+$ (calcd) 227.0822, (obsd) 227.0814.

Triphenylene-Sensitized Photorearrangement of Dimethyl [1-^{2}H]-2-Phenyl-2-propenyl Phosphite (5a). A solution of triphenylene (47.2 mg, 0.207 mmol, 0.0414 M) and dimethyl [1-^{2}H]-2-phenyl-2-propenyl phosphite (**5a**) (332.0 mg, 1.46 mmol, 0.292 M) in C_6H_6 (Photrex) was apportioned and then irradiated for 6 h, after which analysis by ^{31}P NMR showed that about 30% of the starting phosphite had been converted to phosphonate. Flash chromatography gave exclusively dimethyl (*E*)-, (*Z*)-[3-^{2}H]-2-phenyl-2-propenylphosphonate, **6a**. (Spectra were identical with those of phosphonate from PMAP-sensitized photorearrangement of **6a**.)

Triphenylene-Sensitized Photorearrangement of 2-([1-^{2}H]-2-Phenyl-2-propenoxy)-1,3,2−dioxaphosphorinane (5c). A solution of triphenylene (52.6 mg, 0.231 mmol, 0.0462 M) and 2-([1-^{2}H]-2-phenyl-2-propenoxy)-1,3,2-dioxaphosphorinane (**5c**) (141.0 mg, 0.590 mmol, 0.118 M) in C_6H_6 (Photrex) was apportioned and irradiated for 7 days. ^{2}H NMR showed about 40% conversion of **5c** to phosphonate **6c** with complete regioselectivity. Flash chromatography gave exclusively (*E*)-, (*Z*)-2-oxo-2-([3-^{2}H]-2-phenyl-2-propenyl)-1,3,2-dioxaphosphorinane, **6c**. (Spectra of phosphonate **6c** were obtained from 80% ^{2}H-labeled phosphite **5c**.) ^{31}P NMR (121.4 MHz, C_6D_6) δ 21.70; ^{2}H NMR (46.0 MHz, C_6F_6) δ 5.23 (s, br, 0.5 ^{2}H, $C{=}CH^{2}\mathit{H}$), 5.43 (s, br, 0.5 ^{2}H, $C{=}CH^{2}\mathit{H}$) (50:50 mixture of *E* and *Z* isomers); ^{1}H NMR (299.9 MHz, C_6D_6) δ 0.72–0.84 (m, 1 H, $CH_2C\mathit{H}_2CH_2$), 1.00–1.12 (m, 1 H, $CH_2C\mathit{H}_2CH_2$), 2.93 (d, 2 H, $PC\mathit{H}_2$, $^{2}J_{HP} = 22.1$ Hz), 3.26–3.40 (m, 2 H, $CH_2C\mathit{H}_2O$), 3.78–3.92 (m, 2 H, $CH_2C\mathit{H}_2O$), 5.26–5.32 (m, 0.6 H, $C{=}C\mathit{H}^{2}H$), 5.39 (d, 0.6 H, $C{=}C\mathit{H}^{2}H$, $^{4}J_{HP} = 5.3$ Hz), 7.02–7.20 (m, 3 H), 7.36–7.42 (m, 2 H); GC-EIMS (EI −70 eV) *m*/*z* (relative intensity) 239 $[M]^+$ (64), 238 $[M - 1]^+$ (27), 157 (18), 156 (18), 141 (23), 129 (22), 119 (51), 118 (51), 117 (37), 116 (100), 115 (49), 105 (21), 92 (32), 91 (38), 80 (23), 78 (23), 77 $[Ph]^+$ (23), 65 (32), 51 (28), 41 (80). $C_{12}H_{14}2HO_3P$ $[M]^+$: HRMS $[M]^+$ (calcd) 239.0822, (obsd) 239.0818. In a parallel experiment, a 0.1 M benzene solution of **2-([1-^{2}H]-2-phenyl-2-propenoxy)-1,3,2-dioxaphosphorinane** (**5c**) with added *p*-methoxyacetophenone as sentizer was irradiated through Pyrex at 300 nm to give chromatographically isolated phosphonate with a ^{2}H NMR spectrum identical to that from the above triphenylene-sensitized study.

Triphenylene-Sensitized Photorearrangement of 2-([1-^{2}H]-2-Phenyl-2-propenoxy)-1,3,2-dioxaphosphepane (5d). A solution of triphenylene (50.6 mg, 0.222 mmol, 0.0444 M) and 2-([1-^{2}H]-2-phenyl-2-propenoxy)-1,3,2-dioxaphosphorinane (159.0 mg, 0.628 mmol, 0.125 M) in C_6H_6 (5.00 mL, Photrex) was apportioned and irradiated for 5 days (∼40% conversion, ^{31}P NMR). Purification by flash chromatography gave exclusively (*E*)-, (*Z*)-2-oxo-2-([3-^{2}H]-2-phenyl-2-propenyl)-1,3,2-dioxaphosphepane, **6d**. ^{31}P NMR (121.4 MHz, C_6D_6) δ 25.11; ^{2}H NMR (46.0 MHz, C_6F_6) δ 5.22 (s, br, 0.5 ^{2}H, $C{=}CH^{2}\mathit{H}$), 5.42 (s, br, 0.5 ^{2}H, $C{=}CH^{2}\mathit{H}$) (50:50 mixture of *E* and *Z* isomers); ^{1}H NMR (299.9 MHz, C_6D_6) δ 0.91–1.06 (m, 2 H, $C\mathit{H}_2$-CH_2O), 1.08–1.24 (m, 2 H, $C\mathit{H}_2CH_2O$), 2.94 (d, 2 H, $PC\mathit{H}_2$, $^{2}J_{HP} = 22.3$ Hz), 3.26–3.40 (m, 2 H, $CH_2C\mathit{H}_2O$), 3.72–3.87 (m, 2 H, $CH_2C\mathit{H}_2O$), 5.32 (dt, 0.5 H, $C{=}C\mathit{H}^{2}H$, $^{4}J_{HP} = 5.4$ Hz, $^{4}J_{HH} = 1.0$ Hz), 5.40 (d, 0.5 H $C{=}C\mathit{H}^{2}H$, $^{4}J_{HP} = 5.4$ Hz), 7.02–7.20 (m, 3 H), 7.38–

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7.44 (m, 2 H); GC-EIMS (EI −70 Ev) *m/z* (relative intensity) 253 [M]$^+$ (97), 252 [M − 1]$^+$ (6), 199 (52), 198 (30), 143 (21), 119 (80), 118 (50), 117 (39), 116 (100), 115 (36), 97 (20), 92 (42), 78 (19), 77 [Ph]$^+$ (17), 55 (65), 54 (45), 51 (19), 41 (26). $C_{13}H_{16}{}^2H0_3P$ [M]$^+$: HRMS [M]$^+$ (calcd) 253.0978, (obsd) 253.0977.

Benzophenone-Sensitized Photorearrangement of Dimethyl [1-^{2}H]-2-Phenyl-2-propenyl Phosphite (5a). A solution of benzophenone (99.5 mg, 0.546 mmol, 0.109 M) and dimethyl [1-^{2}H]-2-phenyl-2-propenyl phosphite, **5a** (134.9 mg, 0.594 mmol, 0.119 M), in acetonitrile (5.00 mL) was apportioned and irradiated 14 h. Flash chromatography gave exclusively dimethyl (*E*)-, (*Z*)-[3-^{2}H]-2-phenyl-2-propenylphosphonate, **6a**. Spectra were identical to those of phosphonate **6a** from the PMAP-sensitized process.

Benzophenone-Sensitized Photorearrangement of 2-([1-^{2}H]-2-Phenyl-2-propenoxy)-1,3,2-dioxaphosphorinane (5c). A solution of benzophenone (96.0 mg, 0.527 mmol, 0.105 M) and 2-([1-^{2}H]-2-phenyl-2-propenoxy)-1,3,2-dioxaphosphorinane, **5c** (160.2 mg, 0.670 mmol, 0.134 M), in C_6H_6 (5.00 mL) was apportioned and irradiated for 40 h to ∼25% conversion (^{31}P NMR). Flash chromatography gave exclusively (*E*)-, (*Z*)-2-oxo-2-([3-^{2}H]-2-phenyl-2-propenyl)-1,3,2-dioxaphosphorinane, **6c**. Spectra were identical with those of phosphonate **6c** from the triphenylene-sensitized process.

PMAP-Sensitized Photorearrangement of 2-([1-^{2}H]-2-Phenyl-2-propenoxy)-1,3,2-dioxaphosphorinane (5c). Deoxygenated 0.1 M benzene solutions of phosphite in Pyrex tubes also containing 0.2 M and 1.0 M PMAP were irradiated at 300 and 350 nm, respectively. Flash chromatography followed by HPLC (ethyl acetate/ethanol = 9/1) gave **6c** whose ^{2}H NMR spectrum was identical to that of phosphonate **6c** from triphenylene-sensitized photorearrangement.

Direct Irradiation of Dimethyl [1-^{2}H]-2-Phenyl-2-propenyl Phosphite (5a). A 25.0 mL solution of dimethyl [1-^{2}H]-2-phenyl-2-propenyl phosphite (305.6 mg, 1.35 mmol, 0.0540 M) in C_6H_6 (Photrex) was divided equally between three 10 mm quartz tubes and one Pyrex NMR tube. The quartz tubes were stoppered with rubber septa and purged with argon for 10 min. The NMR tube was flame sealed. The solutions were irradiated for 3 h with light from a medium pressure 450-W Hg lamp in a quartz thimble to 100% conversion of **5a** (^{31}P NMR). The products in one of the tubes were isolated by flash chromatography to give, as determined by ^{2}H NMR, a 1:1 mixture of dimethyl (*E*)-, (*Z*)-[3-^{2}H]-2-phenyl-2-propenylphosphonate (**6c**) and dimethyl (*R*,*S*)-[1-^{2}H]-2-phenyl-2-propenylphosphonate (**15c**): ^{31}P NMR (121.4 MHz, C_6D_6) δ 28.97; ^{2}H NMR (46.0 MHz, C_6F_6) δ 2.76 (s, br, 0.5 ^{2}H, $\mathrm{CH^2}H\mathrm{P}$), 5.26 (s, br, 0.25 ^{2}H, $\mathrm{C{=}CH^2}H$), 5.41 (s, br, 0.25 ^{2}H, $\mathrm{C{=}CH^2}H$); ^{1}H NMR (299.9 MHz, C_6D_6) δ 2.84 (m, $\mathrm{PC}H^2\mathrm{HC}$, $^2J_{HP}$ = 22.3 Hz), 2.85 (d, $\mathrm{PC}H_2\mathrm{C}$, $^2J_{HP}$ = 22.2 Hz), 3.30 (d, 6 H, $\mathrm{C}H_3\mathrm{O}$, $^3J_{HP}$ = 10.8 Hz), 5.27−5.33 (m), 5.36−5.43 (m), 7.02−7.15 (m, 3 H), 7.40−7.46 (m, 2 H).

Control Reaction on Scrambling of Deuterium in Dimethyl [3-^{2}H]-2-Phenyl-3-(^{2}H)-2-propenylphosphonate (6a). Deoxygenated solutions in benzene and in cyclohexane, 0.1 M in both **6a** and undeuterated dimethyl 2-phenyl-2-propenyl phosphite, were irradiated in a quartz tube with a 450 W Hanovia medium-pressure lamp. After the phosphite had been nearly totally consumed (24 h), the samples were analyzed by ^{2}H NMR which showed no deuterium attached to C1 in the deuterium-labeled phosphonate.

Thermally-Induced Rearrangement of Dimethyl [1-^{2}H]-2-Phenyl-2-propenyl Phosphite (5a). A 5.00-mL solution of phosphite **5a** (191.4 mg, 0.843 mmol, 0.169 M) in freshly distilled *p*-cymene was divided between two thick-walled Pyrex NMR tubes (∼0.5 mL each) and one 12-mm Pyrex tube (∼4 mL), freeze−thaw degassed, flame-sealed, and then heated to 165−170 °C. After 24 h, approximately 35% of the starting phosphite remained (^{31}P NMR based on total peak areas). Two major phosphonate products were observed in the ^{31}P NMR in a ratio of approximately 5:4 in one tube and 3:2 in another. The major phosphonate (δ^{31}P, 28.95) was the deuterium-labeled 2-phenylallylphosphonate **6a**, and the minor phosphonate (δ^{31}P, 32.72) was dimethyl methylphosphonate. ^{2}H NMR ($\mathrm{C{=}CH^2}H$, δ 5.3, 5.4) showed completely regioselective phosphonate formation (**6a**) along with some side products. Solvent and volatile impurities were removed from the contents of the NMR tube in vacuo (40 °C, 0.05 mmHg). Flash chromatography gave 18 mg (0.08 mmol) of exclusively dimethyl (*E*)-, (*Z*)-[3-^{2}H]-2-phenyl-2-propenylphosphonate (**6a**) (^{2}H NMR). Spectra were identical to those of phosphonate **6a** from PMAP-sensitized photorearrangement.

General Procedure for Determination of Yields of Triphenylene-Sensitized Photorearrangements of 2-Phenylallyl Phosphites. A 2.00 mL solution containing approximately 0.1 mmol each of triphenylene, phosphite, and internal standard (tri-*n*-propyl phosphate) in benzene (Photrex) was apportioned in 0.75-, 0.75-, and 0.50-mL amounts into three Pyrex NMR tubes. All operations between weighings were conducted in an argon-flushed glovebag. After 3 freeze−pump−thaw degassing cycles (0.01 mmHg), the tubes were flame sealed. The two tubes containing 0.75 mL of solution were irradiated with 350-nm lamps in a Rayonet reactor while the third was a control maintained in the dark at 0 °C. The progress of the reactions was followed quantitatively by ^{31}P NMR (decoupler off, 60 s repetition rate). Flash chromatography of the contents of one of the tubes (0.75 mL) on silica gel (100% ethyl acetate) isolated the pure product phosphonate. ^{31}P NMR showed none of the controls to have undergone rearrangement. Phosphonate products were compared spectroscopically to authentic samples of **1a**, **3a**, and **4a** for which independent preparations and spectroscopic and analytical data are given below.

Yields of Phosphonate with Sensitizers Other Than Triphenylene. Appropriately degassed 0.1 M solutions of phosphite with an appropriate amount of benzophenone and internal standard were irradiated under conditions indicated in Table 1. The photorearrangements were monitored by GLC/FID techniques. GLC response factors of phosphite and product phosphonate relative to the internal standard were carefully determined.

(*R*,*S*)-[1-^{2}H]-2-Phenyl-2-propen-1-ol. To a vigorously stirred mixture of activated MnO_2 (90%, Fluka, used as received, 220 g, 2.3 mol) and 250 mL of methylene chloride at 0 °C was added, under nitrogen over a 15-min period, a solution of >98% pure 2-phenylallyl alcohol (10.5 g, 0.078 mol) in 30 mL of methylene chloride. The reaction was allowed to warm to room temperature and then stirred for 3 h. (Longer reaction times were found to be undesirable.) The solution was filtered through a sintered glass frit that was then rinsed with methylene chloride. The filtrate was dried over $MgSO_4$, and the solvent was removed by rotary evaporation. Crude 2-phenyl-2-propenal (∼8 g) was taken up in 40 mL of dry diethyl ether and used in the subsequent reduction.

To 100 mL of dry distilled ether, magnetically stirred under nitrogen, was added 98% ^{2}H-labeled powdered lithium aluminum deuteride (Aldrich, 2.5 g, 0.060 mol). The stirred mixture was cooled to 0 °C, and to it was added, dropwise, the solution of crude 2-phenyl-2-propenal over a 15 min period. The reaction mixture was diluted to 500 mL with ether, quenched with water at 0 °C, and filtered. The filtrate was dried over $MgSO_4$. Solvent removal by rotary evaporation and distillation of the crude reaction mixture gave 3.5 g (0.026 mol, 33% yield) of 97−98% pure ^{2}H-labeled 2-phenylallyl alcohol (normally >98% ^{2}H incorporation by ^{1}H, ^{13}C NMR): ^{2}H NMR (46.0 MHz, C_6H_6) δ 4.18 (d, $\mathrm{CH^2}H\mathrm{OH}$, $^2J_{DH}$ = 1.9 Hz); ^{1}H NMR (299.9 MHz, C_6D_6) δ 1.86 (d, 1 H, $\mathrm{O}H$, $^3J_{HH}$ = 5.6 Hz), 4.22 (s, br, 1 H, $\mathrm{C}H^2\mathrm{HOH}$), 5.26 (m, 1 H, $\mathrm{C{=}C}H_2$), 5.34 (m, 1 H, $\mathrm{C{=}C}H_2$), 7.02−7.16 (m, 3 H), 7.25−7.31 (m, 2 H); ^{13}C NMR (75.4 MHz, C_6D_6) δ 64.33 (t, $C\mathrm{H^2HOH}$, $^1J_{CD}$ = 21.8 Hz), 111.97 ($\mathrm{C{=}}C\mathrm{H_2}$), 126.34, 127.91, 128.61, 139.23 (*ipso*-Ph), 147.82 ($C\mathrm{{=}CH_2}$).

Dimethyl 2-Phenylallyl Phosphite (1). In a glovebag, under a nitrogen atmosphere, dimethyl diethylphosphoramidite (18.6 g, 0.113 mol), 400 mg of 1*H*-tetrazole (0.006 mol), 99% pure (GLC) 2-phenylallyl alcohol (8.4 g, 0.063 mol), and 50 mL of freshly distilled, dry acetonitrile were combined in a 100-mL round bottom flask equipped with a stir bar. The flask was capped with a rubber septum which was replaced outside the glovebag with a nitrogen inlet. The reaction mixture was stirred at room temperature under nitrogen for 10 h and then heated to 30 °C to remove the solvent and remaining phosphoramidite through a vacuum adaptor (0.05 mmHg). The crude product was transferred in a glovebag to a short-path distillation apparatus, and the product mixture was distilled in vacuo (67 °C, 0.02 mmHg) to give three fractions of >99% purity (GLC) (11 g, 0.049 mol, 58% yield) of **1**. When flame-sealed in ampules under nitrogen, phosphites **1**, **3**, and **4** could be stored indefinitely at −10 °C. High-purity 2-phenylallyl alcohol and rigorous exclusion of oxygen are essential to the preparation of pure phosphite, as separation from phosphate contamination cannot be achieved by short-path distillation. Distillation on a long-path column at higher temperatures removed phosphate but led to a small amount of thermal isomerization of the phosphite to the phosphonate: ^{31}P NMR (121.4 MHz, C_6D_6) δ 140.90; ^{1}H NMR (299.9 MHz, C_6D_6) δ 3.29 (d, 6 H, OC*H*$_3$, $^3J_{HP}$ = 10.5 Hz), 4.65 (ddd, 2 H, OC*H*$_2$, $^3J_{HP}$ = 13.6 Hz, $^4J_{HH}$ = 1.2 Hz, $^4J_{HH}$ < 1.0 Hz), 5.40−5.42 (m, 2 H, C═C*H*$_2$), 7.04−7.18 (m, 3 H), 7.28−7.36 (m, 2 H); ^{13}C NMR (75.4 MHz, C_6D_6) δ 48.85 (d, O*C*H$_3$, $^2J_{CP}$ = 9.9 Hz), 63.83 (d, O*C*H$_2$, $^2J_{CP}$ = 12.5 Hz), 113.48 (s, C═*C*H$_2$), 126.37, 128.00, 128.56, 138.77 (*ipso*-Ph), 145.26 (d, *C*═CH$_2$, $^3J_{CP}$ = 4.7 Hz); GC-EIMS (EI −70 eV) *m*/*z* (relative intensity) 226 $[M]^+$ (4), 225 $[M - 1]^+$ (7), 210 $[M\text{-}CH_3]^+$ (5), 131 (63), 130 (52), 129 (20), 118 (37), 117 $[M - (MeO)_2PO]^+$ (47), 116 (26), 115 (100), 109 $[(MeO)_2PO]^+$ (39), 94 (26), 93 (34), 91 (46), 79 (22), 77 $[Ph]^+$ (19), 63 (22), 51 (22); UV $\lambda_{max}(\epsilon)$ 240 (10 295), 280 (291), 290 (112). $C_{11}H_{15}O_3P$ $[M]^+$: HRMS $[M]^+$ (calcd) 226.0759, (obsd) 226.0745. Anal. Calcd for $C_{11}H_{15}O_3P$: C, 58.38; H, 6.69; P, 13.70. Found: C, 58.28; H, 6.67; P, 13.60.

Dimethyl 2-Phenylallylphosphonate (1a). A solution of 3-bromo-2-phenylethene (1.0 g, 0.0051 mol) and trimethyl phosphite (7.0 g, 0.056 mol) was heated to 105 °C. Reaction was accompanied by the evolution of bromomethane. After 0.5 h excess trimethyl phosphite and methylphosphonate side product were removed in vacuo at room temperature. Flash chromatography of the residue on silica gel (98:2 $CHCl_3$−CH_3-OH) gave 450 mg (0.0020 mol, 39% yield) of pure phosphonate **1a** (GLC) as a colorless oil: ^{31}P NMR (121.4 MHz, C_6D_6) δ 29.10; ^{1}H NMR (299.9 MHz, C_6D_6) δ 2.86 (dd, 2 H, PC*H*$_2$, $^2J_{HP}$ = 22.2 Hz, $^4J_{HH}$ = 1.0 Hz), 3.30 (d, 6 H, OC*H*$_3$, $^3J_{HP}$ = 10.8 Hz), 5.30 (ddt, 1 H, C═C*H*$_2$, $^4J_{HP}$ = 5.5 Hz, $^2J_{HH}$ = 1.0 Hz, $^4J_{HH}$ = 1.0 Hz), 5.40 (dd, 1 H, C═C*H*$_2$, $^4J_{HP}$ = 5.5 Hz, $^2J_{HH}$ = 1.0 Hz), 7.04−7.16 (m, 3 H), 7.38−7.44 (m, 2 H). ^{13}C NMR (75.4 MHz, C_6D_6) δ 32.74 (d, P*C*H$_2$, $^1J_{CP}$ = 139.0 Hz), 52.23 (d, O*C*H$_3$, $^2J_{CP}$ = 6.4 Hz), 117.01 (d, C═*C*H$_2$, $^3J_{CP}$ = 10.7 Hz), 126.63, 127.86, 128.49, 139.28 (d, *ipso*-Ph, $^2J_{CP}$ = 10.0 Hz), 141.19 (d, *C*═CH$_2$, $^3J_{CP}$ = 4.6 Hz); GC-EIMS (EI −70 eV) *m*/*z* (relative intensity) 226 $[M]^+$ (54), 225 $[M - 1]^+$ (8), 211 $[M - CH_3]^+$ (10), 131 (74), 130 (60), 129 (26), 118 (31), 117 (24), 116 (25), 115 (100), 109 $[(MeO)_2PO]^+$ (42), 94 (40), 91 (44), 79 (39), 77 $[Ph]^+$ (15). $C_{11}H_{15}O_3P$ $[M]^+$: HRMS $[M]^+$ (calcd) 226.0759, (obsd) 226.0765. Anal. Calcd for $C_{11}H_{15}O_3P$: C, 58.38; H, 6.69; P, 13.70. Found: C, 58.09; H, 6.61; P, 13.89.

Dimethyl (*R*,*S*)-[1-^{2}H]-2-Phenyl-2-propenyl Phosphite (5a). The above procedure for the unlabeled phosphite (**1**) was followed using [1-^{2}H]-2-phenyl-2-propen-1-ol (3.2 g, 0.024 mol), dimethyl diethylphosphoramidite (6.0 g, 0.036 mol), 1*H*-tetrazole (0.300 g, 0.004 mol), and 25 mL of freshly distilled acetonitrile. The crude product was distilled in vacuo (74 °C, 0.05 mmHg) to give, as the purest fraction, 1.5 g (0.0066 mol, 28% yield) of 97% pure phosphite **5a** (GLC): ^{31}P NMR (121.4 MHz, C_6D_6) δ 140.92; ^{2}H NMR (46.0, C_6H_6) δ 4.60 (s, br, OCH^2*H*); ^{1}H NMR (299.9 MHz, C_6D_6) δ 3.29 (d, 6 H, OC*H*$_3$, $^3J_{CP}$ = 10.5 Hz), 4.60−4.69 (m, 1 H, OC*H*^{2}H), 5.39−5.43 (m, 2 H, C═C*H*$_2$), 7.04−7.18 (m, 3 H), 7.28−7.36 (m, 2 H); ^{13}C NMR (75.4 MHz, C_6D_6) δ 48.85 (d, O*C*H$_3$, $^3J_{CP}$ = 9.3 Hz), 63.55 (td, O*C*H^{2}H, $^1J_{CD}$ = 22.3 Hz, $^3J_{CP}$ = 9.9 Hz), 113.54 (s, C═*C*H$_2$), 126.38, 128.00, 128.57, 138.78 (*ipso*-Ph), 145.22 (d, C═*C*H$_2$, $^4J_{CP}$ = 4.7 Hz); GC-EIMS (EI −70 eV) *m*/*z* (relative intensity) 227 $[M]^+$ (5), 226 $[M - 1]^+$ (8), 212 $[M - CH_3]^+$ (4), 132 (67), 131 (70), 130 (33), 119 (46), 118 (57), 117 (30), 116 (100), 115 (31), 109 (50), 95 (23), 93 (45), 92 (47), 91 (23), 79 (27), 77 $[Ph]^+$ (21). $C_{11}H_{14}{}^2HO_3P$ $[M]^+$: HRMS $[M]^+$ (calcd) 227.0822, (obsd) 227.0830.

2-(2-Phenyl-2-propenoxy)-1,3,2-dioxaphosphorinane (3). The procedure for the dimethyl 2-phenylallyl phosphite (**1**) was followed with a slight modification, using 2-phenylallyl alcohol (12.2 g, 0.091 mol), *N*,*N*-diethyl-1,3,2-dioxaphosphorinan-2-amine (22.8 g, 0.13 mol), 400 mg of 1*H*-tetrazole (0.006 mol), and 50 mL of acetonitrile freshly distilled from CaH_2. Complete removal of the excess 1,3,2-dioxaphosphorinan-2-amine after workup by heating the crude product mixture to 60 °C in vacuo (0.05 mmHg) for 2 h was essential to avoid contamination of the distilled phosphite by phosphoramidite. Distillation (103 °C, 0.02 mmHg) gave 14 g (0.058 mol, 65% yield) of **3** (99% pure by GLC). The boiling point of the phosphate is significantly higher than that of the phosphite allowing their separation by distillation. When bath temperatures exceed 130 °C, some thermal isomerization occurs: ^{31}P NMR (121.4 MHz, C_6D_6) δ 131.35; ^{1}H NMR (299.9 MHz, C_6D_6) δ 0.67 (m, 1 H, CH$_2$C*H*$_2$CH$_2$), 1.99 (m, 1 H, CH$_2$C*H*$_2$CH$_2$), 3.30−3.42 (m, 2 H, OC*H*$_2$CH$_2$), 4.08−4.20 (m, 2 H, OC*H*$_2$CH$_2$), 4.58 (m, 2 H, OC*H*$_2$C), 5.38−5.46 (m, 2 H, C═C*H*$_2$), 7.04−7.19 (m, 3 H), 7.28−7.36 (m, 2 H); ^{13}C NMR (75.4 MHz, C_6D_6) δ 28.64 (d, CH$_2$*C*H$_2$CH$_2$, $^3J_{CP}$ = 5.4 Hz), 59.35 (s, CH$_2$*C*H$_2$O, 64.60 (d, O*C*H$_2$C, $^2J_{CP}$ = 20.5 Hz), 113.44 (s, C═*C*H$_2$), 126.41, 127.85, 128.60, 138.80 (*ipso*-Ph), 145.43 (d, *C*═CH$_2$, $^3J_{CP}$ = 5.6 Hz); GC-EIMS (EI −70 eV) *m*/*z* (relative intensity) 238 $[M]^+$ (8), 237 $[M - 1]^+$ (7), 151 −bromo (25), 141 (18), 128 (22), 118 (56), 117 (42), 116 (28), 115 (100), 105 (30), 103 (19), 91 (44), 79 (17), 77 [Ph]+ (32), 65 (30), 51 (22), 41 (63). $C_{12}H_{15}O_3P$ $[M]^+$: HRMS $[M]^+$ (calcd) 238.0758, (obsd) 238.0771. Anal. Calcd for $C_{12}H_{15}O_3P$: C, 60.50; H, 6.35; P, 13.00. Found: C, 60.25; H, 6.18; P, 12.96.

Preparation and Photolysis of 2-(2-Phenyl-2-propenyl)dioxaphospholane (2). Phosphite **2** was prepared in analogous fashion to the above phosphite (**7**) in 46% yield, bp 99−100 °C (0.1 mmHg): ^{31}P ($CDCl_3$) δ 135.2; ^{1}H NMR ($CDCl_3$) δ 7.33 (m, 5 H, C_6H_5), 5.48, 5.36 (2 H, m, C═C*H*$_2$), 4.65 (2 H, m, OCH$_2$), 3.91−4.22 (CH$_2$CH$_2$). A deoxygenated solution 0.1 M in both phosphite and benzophenone was irradiated in a 3-mm Pyrex tube with a 450-W Hanovia light source for 48 h to give less that 1% of the product phosphonate. Under these conditions a parallel solution of dimethyl 2-phenyl-2-propenyl phosphite was totally converted to its phosphonate in 4 h.

2-(2-Phenyl-2-propenoxy)-1,3,2-dioxaphosphepane (4). The above procedure for **1** was followed using 2-phenylallyl alcohol (8.9 g, 0.066 mol), *N*,*N*-diethyl-1,3,2-dioxaphosphepan-2-amine (13.9 g, 0.0727 mol), 1*H*-tetrazole (0.470 g, 0.007 mol), and 50 mL of freshly distilled acetonitrile. Removal of the excess 1,3,2-dioxaphosphepan-2-amine was found to be difficult, even after heating the crude product mixture to 90 °C in vacuo (0.05 mmHg) for several hours. The product mixture was therefore distilled collecting the first fractions containing **4** in a cooled flask (−78 °C). Further distillation gave, as the purest fraction 2.1 g (0.0083 mol, 13% yield) of **4** (104 °C, 0.05 mmHg, 98% pure by GLC) as a colorless oil. Fractions were stored in several flame-sealed ampules under nitrogen. The relatively high boiling point of **4** led to reduced yields because of thermal isomerization of the phosphite: ^{31}P NMR (121.4 MHz, C_6D_6) δ 134.27; ^{1}H NMR (299.9 MHz, C_6D_6) δ 1.24 (m, 4 H, C*H*$_2$CH$_2$O), 3.44−3.58 (m, 2 H, CH$_2$C*H*$_2$O), 3.85−3.99 (m, 2 H CH$_2$C*H*$_2$O), 4.68 (m, 2 H, OC*H*$_2$C), 5.41 (m, 1 H, C═C*H*$_2$), 5.47 (m, 1 H, C═C*H*$_2$), 7.00−7.17 (m, 3 H), 7.26−7.32 (m, 2 H); ^{13}C NMR (75.4 MHz, C_6D_6) δ 30.38 (s, *C*H$_2$CH$_2$O), 63.19 (d, CH$_2$*C*H$_2$O, $^2J_{CP}$ = 2.6 Hz), 64.41 (d, O*C*H$_2$C, $^2J_{CP}$ = 20.5 Hz), 113.51 (s, C═*C*H$_2$), 126.42, 127.96, 128.56, 138.82 (s, *ipso*-Ph), 145.39 (d, *C*═CH$_2$, $^2J_{CP}$ = 5.3 Hz); GC-EIMS (EI −70 eV) *m*/*z* (relative intensity) 252 $[M]^+$ (7), 251 $[M - 1]^+$ (2), 198 (34), 197 (26), 142 (27), 118 (70), 117 (60), 116 (37), 115 (100), 103 (21), 96 (20), 91 (51), 77 $[Ph]^+$ (33), 55 (80), 54 (27), 51 (19). $C_{13}H_{17}O_3P$ $[M]^+$: HRMS $[M]^+$ (calcd) 252.0915, (obsd) 252.0909. A distillation fraction 100% pure by GLC was used for elemental analysis. Anal. Calcd for $C_{13}H_{17}O_3P$: C, 61.90; H, 6.78. Found: C, 61.02; H, 6.88.

Triplet-Quenching Kinetics. Samples were irradiated by 325-nm, 5-ns laser pulses produced by frequency doubling the 650 nm output of a Quanta Ray Model PDL-2 laser, where the dye (DCM, Exciton) was pumped by the second harmonic (532 nm) output of a Quanta Ray Model GCR-2 Nd:YAG laser. The 10 Hz pulse train from the laser is reduced to 0.1 Hz by a mechanical shutter. Average output intensities of 300 and 200 μJ/pulse were used for the photothermal lens and phosphorescence quenching techniques, respectively.

Signal detection and data acquisition for both techniques have been described previously.[36] Briefly, phosphorescence was collected at 90° through an interference notch filter, having a 10 nm pass band centered at 430 nm, and detected with a photomultiplier. Time-resolved photothermal lens signals were detected by aligning a 5-mW HeNe probe laser beam collinearly with the pulsed excitation beam and directing both beams into the sample. Beyond the sample, the probe laser beam was separated from the excitation beam by a dispersing prism, allowed to propagate to the far-field (about 3 m from the sample), and centered on a mask having a radially symmetric, parabolic transmittance profile. The intensity of the radiation passed by the mask,

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(36) Cambron, R. T.; Harris, J. M. *J. Phys. Chem.* **1993**, *97*, 13598.

collected with a lens and focussed onto a photomultiplier, is proportional to the second moment of the probe beam spatial distribution which reports the strength (inverse focal length) of the thermal lens in the sample. Signal transients from both techniques were fit to a first-order kinetic model using nonlinear least-squares to give an observed first order, k_1; this result was employed in the relationship $k_1 = k_o + k_q[Q]$, where k_o is the rate constant for decay in the absence of quencher, k_q is the quenching rate constant, and [Q] is the quencher concentration.

Freshly opened Baker Photrex reagent benzene and EM Science Omnisolve acetonitrile were employed. Benzophenone (50 μM) and triphenylene (40 μM) solutions with varying concentrations (2−40 μM) of α-methylstyrene or phosphite as quenchers were prepared. To avoid oxidation of the phosphite, solutions were prepared in a glovebag with solvents previously purged with argon and using cells fitted with a degassing bulb and a high-vacuum Teflon stopcock. The latter was closed to protect the solutions prior to degassing (6 freeze−thaw−pump cycles at <5 μTorr) and during the quenching experiments. **Benzophenone phosphorescence quenching** in acetonitrile involved three measurements of each signal averaged over 100 transients for each experiment. The measured triplet lifetime in the absence of quencher was 240 ± 10 μs (av of 10 measurements). Triphenylene triplet quenching in benzene and acetonitrile was measured by **photothermal lens spectroscopy**, where three to five replicates of each signal (the average of 100 transients) were acquired. The unquenched triplet lifetimes of triphenylene were determined to be 45 ± 6 μs in benzene solution and 110 ± 16 μs in acetonitrile (average of five measurements); these results are consistent in magnitude with a previously reported result of 55 μs for the triplet lifetime of triphenylene in cyclohexane.[37]

Quantum yields at 335 nm were determined on a Photon Technology International Quanticount electronic actinometer, precalibrated with ferrioxalate, as previously outlined.[38] In these studies, however, the quartz cuvette (quantum yield cell) was modified such that it could be flame sealed following degassing of the sample at $<5 \times 10^{-6}$ mmHg prior to irradiation. Phosphite conversions were less than 6%. Phosphonite formation and phosphite consumption were monitored by GC/FID analysis on a DB-1 capillary column with tri-*n*-phosphate as sensitivity-calibrated internal standard. Other details are found in Table 2.

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Supporting Information Available: Detailed descriptions of the triphenylene-sensitized reactions of **1**, **3**, and **4**; preparations of 2-phenylallyl alcohol, the diethylamino precursors of **3** and **4**, the phosphonates **3a** and **4a**, the deuterated phosphites **5c** and **5d**, phosphites **7** and **8** (6 pages). Ordering information is given on any current masthead page.

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