Photo-Arbuzov Rearrangements of 1-Arylethyl Phosphites: Stereochemical Studies and the Question of Radical-Pair Intermediates

Worawan Bhanthumnavin and Wesley G. Bentrude*

Department of Chemistry, University of Utah, 315 South 1400 East, Salt Lake City, Utah 84112

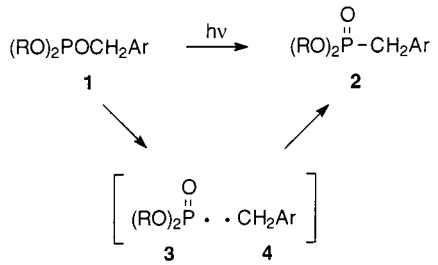
bentrude@chemistry.utah.edu

Received October 31, 2000

The direct UV irradiation of the 1-arylethyl phosphites **7**, **8**, and **9** was carried out in acetonitrile, benzene, and cyclohexane, as was the triphenylene-sensitized reaction of **9**. Dimethyl 1-phenylethyl phosphite, **7**, gives the photo-Arbuzov rearrangement product, dimethyl 1-phenylethylphosphonate (**10**), in 67% average yield and minor amounts (2%) of 2,3-diphenylbutane (**11a**) in quantum yields of 0.32 and 0.02, respectively. The photorearrangement of optically active, predominantly (*R*)-1-phenylethyl phosphite **7** (*R*/*S* = 97/3; 94% ee), at 35−40 °C proceeds with a high degree of stereospecificity at the stereogenic migratory carbon to give predominantly (*R*)-**10** (*R*/*S* = 86/14, 72 ± 2% ee). Use of the nitroxide radical trap TEMPO affords phosphonate **10**, presumably all cage product, from predominantly (*R*)-**7** (*R*/*S* = 97/3; 94% ee) in 64% yield (80% ee, *R*/*S* = 90/10). By contrast, the 1-(4-acetylphenyl)-ethyl phosphite, predominantly (*S*)-**8** (*S*/*R* = 98/2, 96% ee), on direct irradiation gives the corresponding phosphonate (**12**) in only 20% yield along with dimer **11b** in 40% accountability yield. Phosphonate **12** is nearly racemic (*R*/*S* = 52/48). Direct irradiation of predominantly (*R*)-**9** (*R*/*S* = 98/2, 96% ee), a 1-(1-naphthyl)ethyl phosphite, results in a product distribution similar to that from predominantly (*R*)-**7**, but with a somewhat higher degree of retention of configuration in the product phosphonate **13** (*R*/*S* = 93/7, 86 ± 3 ee). By contrast, the triplet triphenylene-sensitized photorearrangement of largely (*R*)-**9** (*R*/*S* = 98/2, 96% ee) leads to product distributions similar to those from direct irradiation of predominantly (*S*)-**8** and is accompanied by almost total loss of stereochemistry in its product phosphonate, **13** (*R*/*S* = 51/49). The partial loss of stereochemistry on direct irradiation of **7** and **9** *provides evidence for radical pair formation*. Furthermore, these stereochemical results are *diagnostic of the multiplicity of the initial radical pair formed*. Values for k_{comb}/k_{rot} for the *proximate* free radical pairs from **7** and **9**, derived experimentally, are severalfold larger than those for the *proximate* singlet pair from $Ph_2C{=}C{=}N{-}CHPhMe$, corrected to 35 °C. The possibility that k_{comb} is increased for the pairs from **7** and **9** is proposed.

Introduction

The photo-Arbuzov rearrangements of arylmethyl phosphites (**1**) to the corresponding arylmethylphosphonates (**2**) upon direct irradiation with UV light have been reported by this laboratory[1−3] and found to be synthetically useful (Ar = phenyl).[4,5] Product,[3] CIDNP,[6] and CIDEP[7] studies of **1** (Ar = Ph, *p*-$MeCOC_6H_6CH_2$, 1-naphthylmethyl) show that these rearrangements proceed largely via radical pair intermediates [**3**,**4**] whose multiplicities depend on whether the phenyl ring is *p*-acetyl-substituted and on whether the photoreaction of the 1-naphthylmethyl phosphite is triplet sensitized. These



radical pairs [**3**,**4**] are of general interest as examples of so-called *proximate pairs*, relatively unusual intermediates that are formed without an intervening molecule (e.g., CO_2, N_2). A classic example is the radical pair generated by the thermolysis of $Ph_2C{=}C{=}N{-}CHPhMe$ that combines to form $Ph_2C(CN)CHPhMe$.[8] Singlet proximate pairs are expected to undergo a high degree of recombination within the solvent cage as shown for **1** (Ar

(1) Omelanczuk, J.; Sopchik, A. E.; Lee, S.-G.; Akutagawa, K.; Cairns, S. M.; Bentrude, W. G. *J. Am. Chem. Soc.* **1988**, *110*, 6908−6909.

(2) Cairns, S. M.; Bentrude, W. G. *Tetrahedron Lett.* **1989**, *30*, 1025−1028.

(3) Ganapathy, S.; Soma Sekhar, B. B. V.; Cairns, S. M.; Akutagawa, K.; Bentrude, W. G. *J. Am. Chem. Soc.* **1999**, *121*, 2085−2096.

(4) Bentrude, W. G.; Mullah, K. B. *J. Org. Chem.* **1991**, *56*, 7218−7224.

(5) Mullah, K. B.; Bentrude, W. G. *Nucleosides Nucleotides* **1994**, *13*, 127−153.

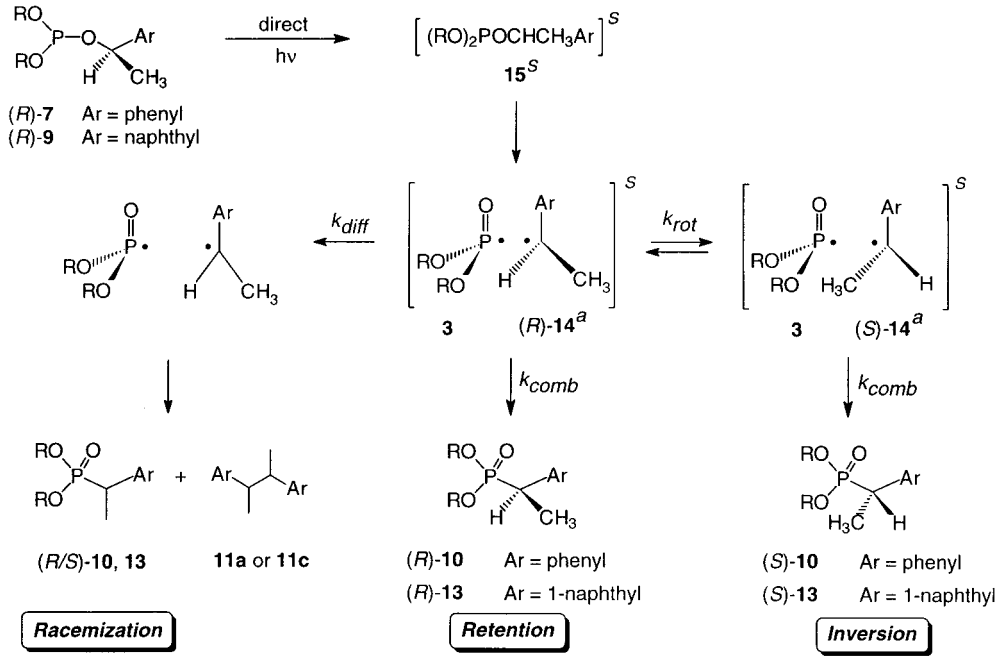
(6) Koptyug, I. V.; Sluggett, G. W.; Ghatlia, N. D.; Landis, M. S.; Turro, N. J.; Ganapathy, S.; Bentrude, W. G. *J. Phys. Chem.* **1996**, *100*, 14581−14583.

(7) Koptyug, I. V.; Ghatlia, N. D.; Sluggett, G. W.; Turro, N. J.; Ganapathy, S.; Bentrude, W. G. *J. Am. Chem. Soc.* **1995**, *117*, 9486−9491.

(8) Lee, K.-W.; Horowitz, N.; Ware, J.; Singer, L. A. *J. Am. Chem. Soc.* **1977**, *99*, 2622−2627.

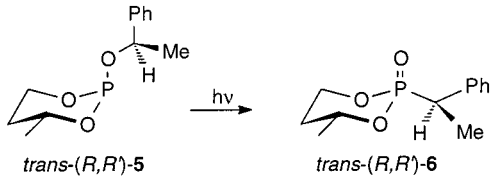
10.1021/jo001545e CCC: $20.00
Published on Web 01/06/2001

Scheme 1[a]



[a] Pro-*R* or pro-*S* orientation of **14**.

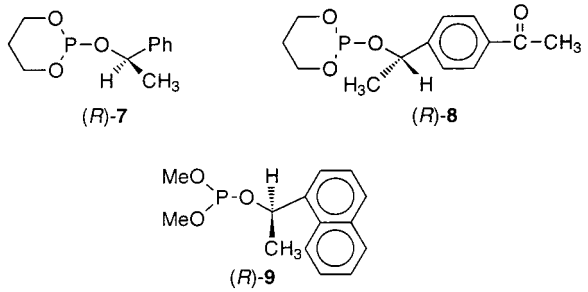
= Ph,[1,2] 1-naphthyl[3,9]) with predominant retention of configuration if a stereogenic migratory carbon center is involved (**5**→ **6**, *direct* irradiation, eq 1).[10]



(1)

Furthermore, the dimethoxyphosphinoyl radicals (**3**) from photolysis of the arylmethyl phosphites (**1**) are closely related structurally to diphenylphosphinoyl radicals [$Ph_2P(O)^{\bullet}$]. The latter are generated on ultraviolet irradiation of acylphosphine oxides which have been used extensively as photoinitiators of radical polymerization.[11] Diarylphosphinoyl radicals have been shown to be highly reactive in radical addition to alkenes and in abstraction reactions[12,13] with rates dependent on radical structure. The demonstrated[6,7] generation from certain **1** of the highly pyramidal (^{31}P hyperfine splitting constant 697 G[7,14]), and therefore highly reactive,[12,13] dimethoxyphosphinoyl radicals (**3**) suggests that **1** and related phosphites are likely to be efficient photoinitiators of polymerization of alkenes, especially electron-rich ones.

We report here investigations of the stereochemistry of certain photo-Arbuzov rearrangements for which production of predominately triplet or, alternatively, singlet pairs can be controlled. To attempt to demonstrate a correlation between stereochemistry at the migratory carbon and the multiplicity of the radical pair, the optically active phosphites (*R*)-2-(1-phenylethyloxy)-1,3,2-dioxaphosphorinane ((*R*)-**7**), (*S*)-2-(1-(4-acetylphenyl)-ethyloxy)-1,3,2 dioxaphosphorinane ((*S*)-**8**), and dimethyl (*R*)-1-(1-naphthyl)ethyl phosphite ((*R*)-**9**) were employed.



A generalized picture of this approach is seen in Scheme 1 for singlet pairs [**3**,**14**] from **7** and **9** and in Scheme 2 for triplet pairs [**3**,**14**].

Indeed, the results reported provide *evidence for discrete singlet radical pair intermediates in the direct irradiation of phosphites* ***7*** *and* ***9***. Furthermore, it is demonstrated that *the stereochemistry at migratory carbon can be correlated with presumed excited-state multiplicity* and that of the radical pairs from optically active **7**−**9** and thus provides a useful assignment criterion, along with product distributions and CIDNP and CIDEP measurements. Indeed, these systems are ideal for measurement of the competition between cage combina-

(9) Bentrude, W. G.; Bhanthumnavin, W.; Ganapathy, S. *Phosphorus, Sulfur, Silicon* **1996**, *109*−*110*, 537−540.

(10) Bhanthumnavin, W.; Bentrude, W. G.; Arif, A. M. *J. Org. Chem.* **1998**, *63*, 7753−7758.

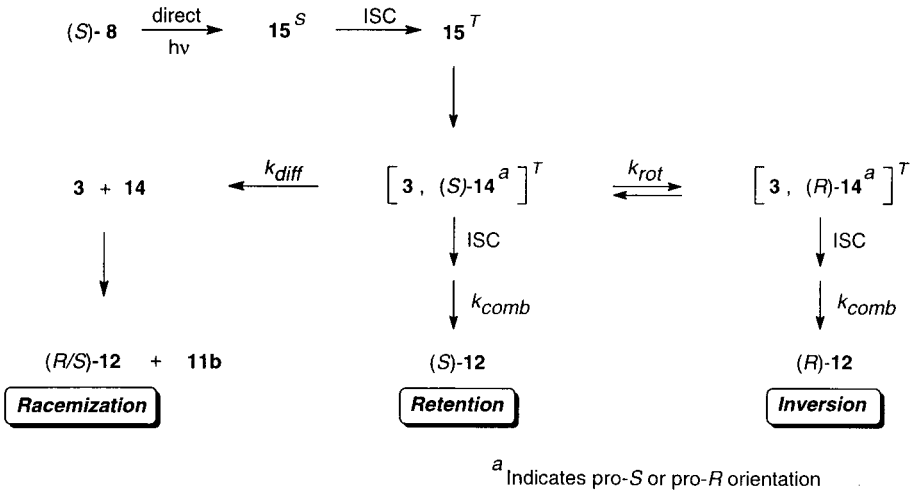
(11) For recent reviews see Dietliker, K. In *Radiation Curing in Polymer Science and Technology;* Fouassier, J.-P., Rabek, J. F., Eds.; Elsevier Applied Science: New York, 1993; Vol. II, p 155. Schnabel, Wl. In *Laser in Polymer Science and Technology: Applications*; Fouassier, J. P.; Rabek, J. F., Eds.; CRC: Boca Raton, 1991; Vol. 2, p 95.

(12) Sluggett, G. W.; McGarry, P. F.; Koptyug, I. V.; Turro, N. J. *J. Am. Chem. Soc.* **1996**, *118*, 7367−7372.

(13) Jockusch, S.; Turro, N. J. *J. Am. Chem. Soc.* **1998**, *120*, 11773−11777.

(14) Davies, A. G.; Griller, D.; Roberts. B. P. *J. Am. Chem. Soc.* **1972**, *94*, 1782. Roberts, B. P.; Singh, K. *J. Organometallic Chem.* **1978**, *159*, 31.

Scheme 2[a]

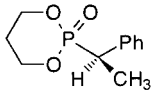


[a] Indicates pro-*S* or pro-*R* orientation.

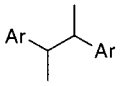
tion (k_{comb}) and rotation (k_{rot}), because we are able to show that combination of **3** and **14** to reform phosphite does not occur. For phosphite **7**, use of the radical scavenger TEMPO allows estimates to be made of relative rate constants for cage combination (k_{comb}) and rotation (k_{rot}) (See Scheme 1) including a very high k_{comb}/k_{rot} value of 11. A minimum value for k_{comb}/k_{rot} of 17 for the radical pair from phosphite **9** is estimated. Both are considerably larger that the same ratio (2.5, CCl_4) reported for the proximate radical pair from $Ph_2C{=}C{=}N{-}CHPhMe$.[8]

Results

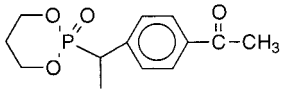
Preparation of 7−9. Isolation of 10−13. Determination of Enantiomeric Ratios. Highly pure phosphites **7**−**9** were prepared in routine fashion from the requisite phosphoramidites and either the optically active alcohols of known configuration and high optical purity or the racemic alcohols. Irradiation of *racemic* **7**−**9** afforded phosphonates **10**, **12**, and **13** and radical dimer **11** that were isolated routinely and characterized spec-



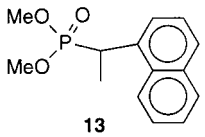
(*R*)-**10**



11a Ar = Ph
11b Ar = *p*-MeCOC$_6$H$_4$
11c Ar = 1-C$_{10}$H$_7$



12



13

troscopically and by elemental analysis. To determine the ratio of enantiomers (*R*/*S*), each optically active phosphite was oxidized to the phosphate by *tert*-butyl hydroperoxide. This reaction is known to be near-quantitative and to occur with *retention of configuration at phosphorus*.[15] The phosphates were purified by HPLC followed by HPLC analysis on a CHIRALCEL OD column and *S* enantiomers baseline-resolved). The ratios of phosphate enantiomers (*R*/*S*) from phosphites **7** and **9** corresponded closely to those of the starting alcohols. Unfortunately, the phosphate enantiomers from **8** were unresolved on chiral HPLC. Unreacted optically active **7** and **9**, at various photoconversions, were similarly oxidized, purified, and analyzed on the chiral HPLC column to determine the *R*/*S* ratio of unreacted phosphite which remained unchanged over the period of the reaction. (See tabulated data in the Supporting Information).

Table 1. Product Yields and Stereochemical Results for the Photoreaction of 7 (*R*/*S* = 97/3)[a]

solvent	conversion of **7** (%)	accountability yield (%)[b] **10**	accountability yield (%)[b] **11a**[c]	*R*/*S* ratio of **10**[d]
acetonitrile	25	64	4.4	86/14
acetonitrile	37	69	4.6	88/12
acetonitrile	78	63	4.0	87/13
cyclohexane	27	63	3.8	88/12
cyclohexane	40	62	4.2	86/14
cyclohexane	57	59	3.8	87/13
benzene	15	67	4.0	86/14
benzene	24	70	3.8	85/15
benzene	48	66	4.2	84/16

[a] Ca. 0.01 M **7**; Rayonet reactor at 35−40 °C. [b] By GC analysis. Based on the amount of consumed **7**. [c] Yield of **11a** doubled to account for the stoichiometry of its formation from **7**. [d] Determined by chiral HPLC on a CHIRALCEL OD column.

Phosphonates **10**, **12**, and **13**, formed on photolysis of *optically active* **7**−**9**, were isolated by HPLC, and their *R*/*S* ratios were determined on a CHIRALCEL OD HPLC column. The predominant enantiomer was assigned the *R* configuration for **10** and **13** and *S* configuration for **12**, based on the primarily retentive stereochemistry determined for the photoreaction of eq 1 (X-ray crystallography)[10] and in an earlier, preliminary study of the photorearrangement of (*R*)-7.[1] Yields of photolysis products (Table 1) were determined by quantitative GC measurements (authentic materials calibrated versus an internal standard). It is important to note that over a wide range of phosphite conversion *no variation in the stereochemical results was noted.*

Photolysis of Optically Active Phosphite 7. Phosphite **7** (ca. 0.01 M) in deoxygenated acetonitrile, benzene, and cyclohexane was irradiated at 35−40 °C through quartz at 254 nm (Rayonet reactor). In Table 1 are recorded phosphonate yields, determined by GC, and

(15) Bentrude, W. G.; Hargis, J. H. *J. Am. Chem. Soc.* **1970**, *92*, 7136−7144.

Table 2. Product Yields and Stereochemical Results for the Photoreaction of 8 (*S*/*R* = 98/2)[a]

solvent	conversion of **8** (%)	accountability yield (%)[b] **12**	accountability yield (%)[b] **11b**[c]	*S*/*R* ratio of **12**[d]
acetonitrile	18	20	42	52/48
acetonitrile	40	19	38	51/49
acetonitrile	97	19	36	50/50
cyclohexane	20	19	40	51/49
cyclohexane	55	20	38	54/46
cyclohexane	93	18	40	52/48

[a] Ca. 0.01 M **8**. Rayonet reactor at 35−40 °C. [b] By GC analysis. Based on the amount of consumed **8**. [c] Yield of **11b** doubled to account for the stoichiometry of its formation from **8**. [d] Determined by chiral HPLC on a CHIRALCEL OD column.

stereochemical data obtained by HPLC (CHIRACEL) from isolated phosphonate **10** at various conversions. Major amounts of **10** (60−70%) are seen. Rather small quantities of dimer **11a** (2%) are found which result from random radical coupling (Scheme 1) of about 4% of the theoretically formed 1-phenylethyl radicals which escape from the original solvent cage. From **7** with *R*/*S* ratio 97/3, the enantiomeric composition (*R*/*S*) of product phosphonate **10** (chiral HPLC) ranges from 84/16 to 88/12 (73 ± 2% ee, avg error). The *quantum efficiencies* of the formation of phosphonate **10** and dimer **11a** were determined in acetonitrile to be 0.32 and 0.02, respectively.

Photorearrangement of Optically Active 8. Direct irradiation of the ketone chromophore (n-π^*) of optically active phosphite **8** (ca. 0.01 M, freeze−pump−thaw degassed, Pyrex tubes) was carried out with light from a 450 W medium-pressure mercury lamp, filtered through a uranium filter sleeve (λ > 320 nm). Table 2 shows the corresponding phosphonate **12** to be formed in approximately 20% yield in both acetonitrile and cyclohexane. Approximately 40% of the 1-arylethyl radicals potentially formed on direct irradiation of **8** are accounted for as dimer **11b** (20% yield; see Scheme 2 to be discussed later). Additional products were detected and identified by GC and GC/MS, but not quantified. These materials are analogous to those found in the reaction of *p*-acetylbenzyl dimethyl phosphite[3,7] and are derived from random free radical coupling. Product phosphonate **12** from optically active **8** (*S*/*R* = 98/2) is seen to be only slightly nonracemic at carbon (average *S*/*R* ratio, 51/49).

Direct Irradiation of Optically Active 1-Naphthylethyl Phosphite 9. Phosphite **9** (ca. 0.01 M in deoxygenated solution) was irradiated at 35−40 °C with light from 300 nm Rayonet lamps through Pyrex in both acetonitrile and cyclohexane solvents. In Table 3 product distributions similar to those from photorearrangement of phosphite **7** are seen. In both solvents 60−70% yields of phosphonate **13** resulted. 2,3-Dinaphthylbutane (**11c**) (*meso*/*d*,*l* = 1/1) accounts for 2−5% of the potentially formed 1-naphthylethyl radicals (Scheme 1). Compared to phosphite **7**, a somewhat higher degree of retention of configuration at the migratory carbon is observed. Thus phosphite **9** (*R*/*S* = 98/2) gives the enantiomeric phosphonates in *R*/*S* ratios ranging from 91/9 to as high as 95/5 (86 ± 3% ee, avg error).

Triplet-Sensitized Reactions of Phosphite 9. The easily accessible triplet state (T_1) of triphenylene (E_T = 67 kcal/mol[16]), and its UV absorption at relatively long

Table 3. Product Yields and Stereochemical Results Obtained from Direct Irradiation and Triphenylene-Sensitized Photoreactions of Phosphite 9 (*R*/*S* = 98/2)[a]

conditions	solvent	conversion of **9** (%)	accountability yield (%)[b] **14**	accountability yield (%)[b] **11c**[c]	*R*/*S* ratio of **14**[d]
direct $h\nu$	acetonitrile	14	65	4.6	91/9
direct $h\nu$	acetonitrile	39	72	4.6	92/8
direct $h\nu$	acetonitrile	92	60	3.8	94/6
direct $h\nu$	cyclohexane	15	69	2.2	94/6
direct $h\nu$	cyclohexane	36	63	2.0	95/5
direct $h\nu$	cyclohexane	95	61	3.4	92/8
sens.	acetonitrile	14	21	40	52/48
sens.	acetonitrile	45	20	40	51/49
sens.	acetonitrile	92	19	42	51/49

[a] Ca. 0.01 M **9**. 0.02 M triphenylene. Rayonet reactor at 35−40 °C. [b] By GC analysis. Based on the amount of consumed **9**. [c] Yield of **11c** doubled to account for the stoichiometry of its formation from **9**. [d] Determined by chiral HPLC on a CHIRALCEL OD column.

wavelengths (> 340 nm), make triphenylene an appropriate triplet sensitizer for the 1-naphthylethyl chromophore (450 W medium-pressure mercury lamp, uranium glass filter, 320 nm cutoff). Phosphite (*R*)-**9** in deoxygenated acetonitrile (*R*/*S* = 98/2, ca. 0.01 M) also containing triphenylene (ca. 0.02 M) was sealed in Pyrex tubes under vacuum. The reaction occurred quite slowly, presumably because the light was filtered, to give the results in Table 3. At all conversions, the corresponding phosphonate is formed in 20 ± 1% yield, along with 2,3-dinaphthylbutane (**11c**) in about 20% yield (40% accountability of 1-naphthylethyl radicals, potentially generated from **9**). Product phosphonate **13** is formed with a slight excess of the *R* isomer present at all three conversions (chiral HPLC, multiple injections at each conversion). A control sample of phosphite **9** (ca. 0.01 M) did not undergo reaction on irradiation in the absence of triphenylene.

Photolysis of Optically Active Phosphite 7 in the Presence of TEMPO. The stable radical TEMPO is often used to scavenge free radical pairs that escape the initial solvent cage and appeared applicable to the study of the photolysis of **7**. However, irrradiation of TEMPO can lead to hydrogen abstraction by its excited state.[17] This side reaction was minimized by doing the trapping studies in cyclohexane where GC showed the formation of minor amounts of abstraction product (TEMPO-H) to be less than in acetonitrile. Although an excess of TEMPO was employed, its concentration was held relatively low to minimize the "anti-scavenger effect" of TEMPO noted by Turro et al.[18] A detailed accounts of radical-trapping approaches used during photolysis of related arylmethyl phosphites was published earlier.[3]

Solutions of phosphite **7** (ca. 0.01 M, *R*/*S* = 97/3) were irradiated in cyclohexane at 254 nm in the presence of a range of concentrations of TEMPO (0.002−0.022 M). Yields and enantiomeric ratios of phosphonate **10** are shown in Table 4. Results obtained in the absence of TEMPO are also included for comparison. The amounts of 2,3-diphenylbutane, the product formed from random coupling of 1-phenylethyl radicals (Scheme 1), decreases to zero at 0.015 M TEMPO concentration. Concomitantly, the yield of product phosphonate **10** decreases slightly

(16) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

(17) Johnston, L. J.; Tencer, M.; Scaiano, J. C. *J. Org. Chem.* **1986**, *51*, 2806−2808.

(18) Step, E. N.; Buchachenko, A. L.; Turro, N. J. *J. Am. Chem. Soc.* **1994**, *116*, 5462−5466.

Table 4. Photolysis of 7 (*R*/*S* = 97/3) in the Presence of TEMPO[a]

7/TEMPO	conversion of **7** (%)	accountability yield (%)[b] **10**	accountability yield (%)[b] **11a**[c]	*R*/*S* ratio of **10**[d]
e	15	67	4.0	86/14
e	24	70	3.8	85/15
e	48	66	4.2	86/14
1:0.4	23	68	3.8	85/15
1:0.6	20	66	3.0	86/14
1:0.8	16	68	2.0	88/12
1:1.0	17	67	0.8	89/11
1:1.5	20	67	0	90/10
1:1.8	19	64	0	89/11
1:2.0	22	65	0	90/10
1:2.2	20	64	0	90/10

[a] Ca. 0.01 M **7**, cyclohexane solvent. Rayonet reactor at 35−40 °C. [b] By GC analysis. Based on the amount of consumed **7**. [c] Yield of **11a** doubled to account for the stoichiometry of its formation from **7**. [d] Determined by chiral HPLC on a CHIRALCEL OD column. [e] No TEMPO added.

and levels off at approximately 65%. Moreover, as the concentration of the trap increases, a higher degree of retention of configuration at the migrating carbon is observed in the product phosphonate, and the reproducible enantiomeric composition of **10** increases to a constant value (90/10 *R*/*S*; 80% ee). These results indicate that total scavenging of cage-free radicals has occurred.

GC and GC/MS analysis showed the presence of TEMPO-H and TEMPO-cyclohexyl resulting from hydrogen abstraction from the cyclohexane solvent by electronically excited TEMPO. However, neither of the products of trapping of 1-phenylethyl radical or phosphinoyl $(MeO)_2P(O)^{\bullet}$ by TEMPO was detected by GC/MS analyses. It not surprising that products from radical trapping by TEMPO could not be detected by GC and GC/MS analyses on irradiation of phosphite **7**. The reaction for the 4-keto analogue of TEMPO with resonance-stabilized carbon-centered radicals is thermally reversible even at ambient temperatures, and the 1,1-diphenylethyl radical/TEMPO adduct decomposes slowly even at 20 °C ($k_1 = 4.4 \times 10^4$ M^{-1} s^{-1}, $k_{-1} = 3.5 \times 10^4$ M^{-1} s^{-1}).[19,20] In a hot GC inlet and column, these decomposition processes surely become even more significant. Literature reports[21,22] of trapping of phosphinoyl radicals by TEMPO do not discuss the thermal stability of the trapping products.

From the photolysis of phosphite **7** in the presence of TEMPO, one might expect to observe the product $(MeO)_2P$-(O)-TEMPO by ^{31}P NMR, as is reported in the photolysis of **1** with Ar = *p*-$MeCOC_6H_4$ at δ 6.7.[3] (The ^{31}P NMR chemical shift for the analogous trapping product using a closely related nitroxyl radical is 4.94.[22]) However, a distinct peak in the expected region that could be clearly assigned to $(MeO)_2P(O)$-TEMPO was not found because of low peak intensities, low signal-to-noise, and the presence of several peaks in the expected chemical shift region.

Stereochemical Control Experiments. Solutions of optically active phosphonates **10**, **12**, and **13**, irradiated at concentrations such as those used in the stereochemical studies, were shown by chiral HPLC to have unchanged *R*/*S* ratios over irradiation periods similar to those employed in the stereochemical studies. Furthermore, when these phosphonates were subjected to the entire workup procedure, their enantiomeric compositions were unchanged.

Discussion

Tables 1−4 display data from the irradiation of phosphites **7**−**9** that demonstrate the essential invariance of the results as a function of conversion. These data are condensed and summarized in Table 5 for ease of comparison. In addition, the last few columns of Table 5 list stereochemical results derived, as set forth later, from the *R*/*S* ratios of reactants and products found in Tables 1−4. Optically active phosphites **7**−**9** will be seen to give product distributions and stereochemistries at the stereogenic carbon, strongly dependent on whether the photorearrangement proceeds from a triplet or singlet excited state. These results will be discussed by reference to Schemes 1 and 2. Scheme 1 depicts the reaction alternatives and stereochemical options for a *singlet* radical pair [**3**,**14**] formed from a singlet excited state (**14**$^{\mathbf{S}}$). Scheme 2 is an analogous treatment for radical pairs that are initially *triplet*. The essentially planar 1-arylethyl radicals (**14**) are either pro-*R* or pro-*S*, depending on whether rotation (k_{rot}) has occurred. Combination of pairs [**3**,**14**] within the initial solvent cage (k_{comb}) affords phosphonate with either *retained* or *inverted* configuration at the stereogenic carbon center of the carbon free radical with the degree of retention at carbon dependent on the relative values of k_{comb} and k_{rot}. Cage combination (k_{comb}) to form phosphonate competes with diffusive separation (k_{diff}) which generates cage-free pairs that on combination yield phosphonate of *racemic* (*R*/*S*) composition.

Before discussing stereochemistry in detail, it must be strongly emphasized (as detailed in the Results section) that the stereochemical integrities of both **7** and **9** are completely preserved during photoreaction, whether on *direct* irradiation of **7** and **9** or on *triplet sensitization* of **9**. The enantiomeric excess of phosphite measured on the phosphate, at a range of conversions, remain within ca. 2−3% of that prior to irradiation. (See Results section and Supporting Information, Tables 1 and 2). This finding will be presumed to apply also to phosphite **8**, whose phosphate enantiomers overlapped on chiral HPLC. The phosphonates themselves similarly retain their stereochemical integrity on photoirradiation. Thus, the loss of configuration at stereogenic carbon in phosphonates **10**, **12**, or **13** must occur *following* formation of the presumed radical pairs [**3**,**14**] of Schemes 1 and 2.

Furthermore, the stereochemical integrity of the starting phosphites means that *the radical pair [**3**,**14**] does not recombine to regenerate phosphite*. Thus, on direct irradiation of **7** and **9**, some loss of initial phosphite stereochemistry is seen in the product phosphonates **10** and **13** (Table 5). Presuming that this results (as discussed subsequently) from combination of caged radical pairs [**3**,**14**] following rotation of the prochiral 1-arylethyl species (**14**), recombination of **3** and **14** to reform phosphite, were it to occur, must do so with some loss of stereochemistry at carbon. This conclusion applies as well to triplet sensitization of the reaction of **9** where stere-

(19) Grattan, D. W.; Carlsson, D. J.; Howard, J. A.; Wiles, D. M. *Can. J. Chem.* **1979**, *57*, 2834−2842.
(20) Howard, J. A.; Tait, J. C. *J. Org. Chem.* **1978**, *43*, 4279−4283.
(21) Baxter, J. E.; Davidson, R. S. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 311−314.
(22) Busfield, W. K.; Grice, I. D.; Jenkins, I. D. *Aust. J. Chem.* **1995**, *48*, 625−634.

Table 5. Summary of Photochemical Results

compound	conditions	accountability yield (%) phosphonate	accountability yield (%) dimer [a]	cage yield phosphonate (%)	100y[d]	% net retention[c]	k_{comb}/k_{rot}
7	direct $h\nu$	67 ± 2[b]	4	*e*	88 ± 2[b]	74	6[c] 7[d]
7	with TEMPO	64	0	65	93	82	9[c] 13[d]
8	direct $h\nu$	19 ± 1	38 ± 2	*e*	*f*	4	0.1[c]
9	direct $h\nu$	65 ± 4	3 ± 1	*e*	95 ± 2[b]	88	15[c] 19[d]
9	sens.	20 ± 1	40	*e*	*f*	2	0.04[c]

[a] Yield of dimer doubled to account for the stoichiometry of its formation from starting materials. [b] Average deviation from average. [c] Method I. [d] Method II. [e] TEMPO not added. Cage yield not applicable. [f] Method II not applicable.

ochemical integrity is almost totally lost in the product phosphonate (**13**). To the extent that initially formed triplet radical pairs might live long enough in the solvent cage to intersystem cross and recombine, considerable loss of stereochemistry in phosphite **9** formed on recombination would be expected. However, this affect would be attenuated in that only a small yield of cage products of any type is expected from triplet pairs, as is discussed later. That the pair [**3,14]** does not combine to regenerate phosphite will be assumed to apply as well to the photorearrangement of **8** whose phosphates were inseparable by chiral HPLC analysis.

Analysis of Stereochemical Results. The stereochemical results (Tables 1−4) can be analyzed in terms of the radical-pair [**3**,**14**] of Scheme 1 by two approaches (methods I and II) that give comparable results. Let R_{SM} and S_{SM} be the percentage of *starting phosphite* in the *R* and *S* configurations, respectively, and R_{obsd} and S_{obsd} represent the percentage of the observed *product phosphonate* in the *R* and *S* configurations. Method I is modeled after the published work on the stereochemically analogous thermal rearrangement via singlet radical pairs of optically pure (*S*)-MePhCH−N=C=CPh$_2$ reported by Singer et al.[8] The steady-state kinetic treatment on the radical pair from the ketenimine was based on a scheme entirely parallel to Scheme 1 with the assumption that the rotation of radical **14** (1-phenylethyl in both systems) is *reversible*. Thus, starting with stereochemically pure (*R*)-phosphite, the steady-state approximation for the concentration of radical pair [**3**,**14**] is applied to give eq 2 and from it eq 3:

$$R_{obsd}/S_{obsd} = (k_{comb} + k_{rot})/k_{rot} \quad (2)$$

and from eq 2

$$k_{comb}/k_{rot} = R_{obsd}/S_{obsd} - 1 \quad (3)$$

Equation 2 is simpler than its equivalent published in ref 8 in its derivation in that formation of phosphonate by combination of cage-free pairs is neglected; i.e., the assumption is made that k_{diff} is negligible compared to the sum $k_{comb} + k_{rot}$. This simplification is needed since we do not have the otherwise necessary accurate measure of the fraction of products, *f*, that escape the solvent cage ($f = k_{diff}/(k_{comb} + k_{diff})$) even for (*R*)-**7**, because of the lack of total product accountability discussed elsewhere in this paper. The neglect of k_{diff} appears justified by the small amount of 1-arylethyl radical dimers (**11a** and **11c**) found and the small change in both yield of phosphonate **10** and overall stereochemistry noted when TEMPO is added to the photolysis of (*R*)-**7**.

Unfortunately, in the phosphite photoreaction systems, pair [**3**, (*S*)-**14**] is formed not only by rotation within the pair [**3**,(*R*)-**14**] formed from (*R*)-**7** or (*R*)-**9** (Scheme 1) but also by photolysis of the 2−3% of the minor enantiomers, (*S*)-**7** and (*S*)-**9**. However, to a close approximation, one still can apply eq 2 by simply correcting the amount of (*S*)-**10** or (*S*)-**13** reported in the Tables 1, 3, and 4 for the 2−3% of phosphonate formed from *S* phosphite as demonstrated below. Equation 3 then yields the ratio k_{comb}/k_{rot}. Furthermore, net retention at carbon, an empirical quantity not based on a presumed mechanism, is derived in the usual fashion from eq 4:

$$\%\ \text{net retention} = (R_{obsd} - S_{obsd})/(R_{obsd} + S_{obsd}) \quad (4)$$

In this approach (method I) for phosphite (*R*)-**7**, the observed ratio R_{obsd}/S_{obsd} of 90/10 for the TEMPO-scavenged photolysis (Table 4) is changed to 90/8 by subtraction of the approximately 2% of (*S*)-**10** generated from (*S*)-**7** to give a percentage ratio of 91/9. From eq 3, $k_{comb}k_{rot} = 9$. Percent net retention = 100(91−9)/100 = 82. These parameters for photolysis of phosphites **7**−**9** are recorded in Table 5.

In Method II it is noted first that on *direct* irradiation of **7** and **9**, *the degree of retention of configuration at the stereogenic carbon in phosphonates **10** and **13** is very high*. Therefore, as a simplifying approximation, it can be assumed that the initially formed pro-*R* radical **14** will either combine to give *R* phosphonate or undergo only a *single* rotation before radical combination to yield *S* phosphonate. The same assumption of course applies to the [**3**, (*S*)-**14**] radical pairs from phosphite of *S* configuration. In this approach neither the *R* nor the *S* form of the starting phosphite is ignored, and Scheme 1 would be expanded to include *direct generation* of the pair [**3**,(*S*)-**14**] from (*S*)-**7** and (*S*)-**9**. Clearly, the assumption that $k_{comb} \gg k_{rot}$ is not valid for the direct photolysis of phosphite **8** or the triplet sensitized photolysis of **9** for which stereochemistry is nearly completely lost. Method II, therefore, is not applicable to those photoreactions.

By Method II if *y* equals the fraction of the initial radical pair [**3**,**14**] from R_{SM} or S_{SM} that combines before rotation of **14** to give product phosphonate with retention of configuration, then $1 - y$ is the fraction of R_{SM} or S_{SM} that yields product phosphonate with *inverted* configuration at the stereogenic carbon. It is then obvious that the total amount of each enantiomer to be formed (R_{obsd} or S_{obsd}) is given by eqs 5 and 6.

$$R_{obsd} = R_{SM}y + S_{SM}(1 - y) \quad (5)$$

$$S_{obsd} = S_{SM}y + R_{SM}(1 - y) \quad (6)$$

These equations are readily solved to give eq 7 from which *y* can be obtained. The quantity *y*, *the fraction of initially formed reaction pairs that combine with retention*

of configuration at the chiral center of starting phosphite, is given in Table 5 for phosphites **7** and **9** on a percentage basis as 100*y*:

$$y = (R_{obsd} - S_{SM})/(R_{SM} - S_{SM}) = (R_{obsd} - R_{SM} - 100)/(2R_{SM} - 100) \quad (7)$$

For example, under TEMPO-scavenging conditions, the photoreaction of phosphite **7,** 97% of which is in the *R* configuration at the stereogenic carbon, yields phosphonate **10** that is 90% *R* in composition, corresponding to *y* = 0.93 (eq 7). The value of 100*y* (93) is different from the % net retention obtained from eq 4 (method I), a number obtained without regard to mechanism.

For method II the relationship between the rate constant for rotation (k_{rot}) and the rate constant for recombination (k_{comb}) simply corresponds (eq 8) to the fraction of radical pairs within the initial solvent cage of the starting material that undergoes recombination before rotation has occurred divided by the fraction that undergoes recombination after rotation:

$$k_{comb}/k_{rot} = y/(1 - y) \quad (8)$$

Therefore, for the radical system discussed above from phosphite **7** with added TEMPO ($y = 0.93$), $k_{comb}/k_{rot} = 0.93/(1.00-0.93) = 13$ (Table 5). Thus, radical pair [**3**, **14**] is 13 times more likely to combine than to undergo rotation followed by combination. Methods I and II are seen in Table 5 to give very similar results for k_{comb}/k_{rot}.

Direct Photolysis of Phosphites 7 and 9. As shown in Tables 1, 3, 4, and 5, photorearrangements of the 1-arylmethyl phosphites **7** and **9**, triggered by direct irradiation, give the corresponding phosphonates in 60−70% yields. When TEMPO is added (Tables 4), the yield of phosphonate **10**, exclusively cage product, is slightly reduced to 65% compared to 67% in its absence. Only 3−4% of the potentially formed 1-arylethyl radicals (**14**, Schemes 1 and 2) are accounted for as 2,3-diarylbutanes (Tables 1, 3, and 4). Thus, the majority of phosphonates **10** and **13** is formed within the reaction cage. The measured quantum yield, ϕ_P, for formation of phosphonate **10** from **7** of 0.32 is close to that for phosphonate generation from **1** (Ar = Ph) of 0.43.[3] *These results show the photo-Arbuzov rearrangements of arthylmethyl and 1-arylethyl phosphites to be reasonably efficient processes.*

A very high degree of combination of the *initial pair* with retention of configuration at the stereogenic carbon (100y, method I) is seen: for **7**, 88 ± 2% without scavenger added and 93% with sufficient levels of added TEMPO (≥0.015 M); for **9**, 95 ± 2% unscavenged. The corresponding percent net retention values (method II), 74, 82, and 88 for phosphites **7** and **9**, show the same systematic increase in stereospecificity with structure as the 100*y* parameters.

From eqs 2 and 8, k_{comb}/k_{rot} for the radical pair from **9** is estimated to be 15 and 19 (methods I and II, respectively, avg 17). These are *minimum* values, since a small portion of phosphonate **13** (no added TEMPO) arises via combination of free pairs to yield racemic **13**. On the basis of comparisons of averaged k_{comb}/k_{rot} values for **7** and **9** from *unscavenged* photoreactions (7 and 17, respectively), and the assumption that k_{comb} is essentially the same for the radical pairs from **7** and **9**, it appears that the 1-naphthylethyl radical undergoes rotation more slowly than its 1-phenylethyl counterpart. This difference may arise from the somewhat larger steric size of the 1-naphthylethyl radical which gives rise to larger rotational correlation time.

Approximately 35% of the phosphinoyl radicals potentially formed in the photorearrangements of **7** and **9** is unaccounted for. Numerous side products are formed in small quantities, as shown by ^{31}P NMR spectroscopy, but were not examined further because of their number and our primary interest in reaction stereochemistry. Formation of unidentified products of coupling of the radical pair by attack of the phosphinoyl radical at the ring carbons of the naphthyl ring may occur. Indeed, a recent paper reports[23] the coupling at the *ortho* and *para* carbons as well as the benzylic carbon for the radical pair [$Ph_2P(O)^{\bullet}$ $^{\bullet}CH_2Ph$] that is formed photolytically from $Ph_2P(O)CH_2$ Ph. The formation of side products and the trapping of radical diffusion products by benzene solvent on photolysis of **1** (Ar = Ph) was discussed in an earlier paper.[3] The failure to observe a prominent peak assignable to $(MeO)_2P(O)$-TEMPO in the ^{31}P NMR spectrum of products from irradiation of phosphite **7** solutions with TEMPO added supports the conclusion that *cage-free radicals are not generated in large amounts, as is also indicated by low yields of products from the dimerization of 1-arylmethyl radicals.* Disproportionation of the radical pair [**3**,**14**] is a further cage process available to the 1-arylethyl phosphites but not to arylmethyl phosphites (**1**). However, ^{31}P NMR or GC evidence for formation of $(MeO)_2P(O)H$ in measurable amounts, likely >5%, was not found.

Comparisons to Other Photo-Arbuzov Systems. The published study[10] of the stereochemistry of the photorearrangement of *trans*-**5** showed a similar but slightly lower degree of retention at stereogenic carbon ($100y \approx 80$) in an *unscavenged* reaction. Unscavenged accountability yields of phosphonate from direct irradiation of the benzyl phosphite analogous to **9** (**1**, Ar = Ph) range from 67 to 81% in acetonitrile, cyclohexane, and benzene,[3] and accountabilities of benzyl radicals as bibenzyl are generally 6−8%. The naphthyl analogue of **7** and **9** (**1**, Ar = 1-naphthyl) was found[24] to give 71% and 74% accountability yields of phosphonate in cyclohexane and benzene, respectively, that are reduced by 5−10% by the addition of *tert*-BuBr which scavenges the cage-free phosphinoyl radicals to form $(MeO)_2P(O)$-Br.[24]

The Question of Ion-Pair Intermediates. The possibility that these singlet photoprocesses involve ion pairs was addressed in a previous publication[3] on the photochemistry of phosphite **1** with Ar = Ph and Ar = *p*-$MeCOC_6H_4$. It was discounted on the basis of the lack of effect on product distribution and trapping results of changing the solvent from benzene to highly polar acetonitrile. Unpublished results[25] showing the lack of systematic effect of substituents on the group Ar (Ph and 1-naphthylmethyl) of **1** and the failure to trap ion pairs with added MeOH were also cited. The lack of effect of solvent polarity on these reactions (Tables 1, 3, and 4) is further emphasized by the consistency of the stereochemical outcome in polar acetonitrile as well as in nonpolar cyclohexane and benzene. The lifetimes of ion pairs, and

(23) Zhao, N.; Neckers, D. C. *J. Org. Chem.* **2000**, *65*, 2145−2150.
(24) Bentrude, W. G.; Ganapathy, S.; Somasekhar, B. B. V. Unpublished results.
(25) Bhanthumnavin, W. Unpublished results from this laboratory.

their ability to lose stereochemical integrity before combination, might be expected to respond to changes in solvation.

Comparisons to Related Radical-Pair Systems. A classic study of a singlet *proximate* radical pair system (no intervening molecule, e.g., CO_2, N_2) is the thermolysis at 60 °C of $Ph_2C{=}C{=}NCHPhMe$ which was done both with and without added scavengers.[8] The coupling product $Ph_2C(CN)CHPhMe$ was formed in ≥95% chemical yield (unscavenged). Scavenging established cage yields of nitrile of 62 and 75% in acetonitrile and CCl_4, respectively. The reported[8] k_{comb}/k_{rot} values of 2.5 (CCl_4) and 1.3 (acetonitrile) for the ketenimine system suggest that if k_{comb} is similar for the proximate pairs from phosphite **7** and the ketenimine, then k_{rot} for the 1-phenylethyl radical (**14**) in the ketenimine system is somewhat *larger* than it is in the radical pair [**3**,**14**] formed from phosphite **7** (k_{comb}/k_{rot} = 11, avg). An increased k_{rot} value might result at least in part from the ketenimine reaction being studied in a solvent of lower viscosity and/or from the higher temperature (60 °C) at which the system was investigated. Indeed, viscosity differences between CCl_4 and acetonitrile are most probably responsible for the approximate 2-fold decrease in the ratio k_{comb}/k_{rot} determined at 60 °C in the investigation of $Ph_2C{=}C{=}NCHPhMe$, as suggested by the authors of that paper.[8]

The ratio k_{comb}/k_{rot} (11, avg value) for the radical pair from phosphite **7** (TEMPO added) was measured at 35−40 °C in cyclohexane, which has a viscosity (1.02 cp, 17 °C) close to that of CCl_4 (1.04 cp, 20 °C). However, at 60 °C, where the study of $Ph_2C{=}C{=}NCHPhMe$ was done, the viscosity of CCl_4 is reduced to 0.58 cp[8] which consequently would increase k_{rot} (essentially rotational diffusion) for the 1-phenylethyl radical. The viscosity related expected increase in k_{comb}/k_{rot} at 35 °C, compared to the value at 60 °C (2.5) (k_{comb} assumed invariant with temperature), can be estimated from the expression $(\eta^{-\alpha_{T1}}/\eta^{-\alpha_{T2}})$, where η is the viscosity at T_1 or T_2, and α is a constant, normally one or less.[26] (In other words, k_{rot} is inversely proportional to viscosity to the power α.[26]) The maximal effect of temperature decrease from 60 °C, at which the radicals from $Ph_2C{=}C{=}NCHPhMe$ were studied, to 35° C where the investigations of phosphite **7** were done, results for $\alpha = 1$. Using the reported value for η for CCl_4 at 60 °C (0.58 cp) and an interpolated value[27] at 35 °C (0.81 cp), the reported ratio k_{comb}/k_{rot} for the 1-phenylethyl radicals from $Ph_2C{=}C{=}NCHPhMe$ would be increased to (0.81/0.58)(2.5) or 3.5. This small increase from 2.5 to 3.5 still allows for a severalfold increase in k_{comb} for the 1-phenylethyl radical from photolysis of phosphite **7** (k_{comb}/k_{rot} = 11, avg value).

It seems likely, though still quite speculative, that k_{comb} is increased for the pair [**3**,**14**], because it involves a radical, $(MeO)_2P(O)^{\bullet}$, which has a SOMO with a high degree of *s* character. Changes in rate constants of second-order reactions of a series of phosphinoyl radicals, $X_2P(O)^{\bullet}$, have been correlated with variations in SOMO *s* character.[12,13,28] Measurable variations in rate constants for radical coupling reactions, which are already of the order of those for diffusion, may seem unusual. However, the so-called *proximate* free radical pairs under discussion are formed in singlet reactions which are on the mechanistic border between radical pair formation and truly concerted processes. Thus, in addition to effects of hybridization, very small changes in the initial proximity of pairs, perhaps engendered by steric factors, may give rise to changes in k_{comb}. Though steric effects on radical combination are well-known, we are unaware of studies correlating variations in radical hybridization with rates of coupling (k_{comb}) of caged pairs. An increased k_{comb} means that, as was argued earlier, the yield of cage products from photolysis of **7** and **9** should be higher than the experimental yields of phosphonates **10** and **12**.

Most importantly, the relatively high k_{comb}/k_{rot} values found for the ketenimine system, and for **7** and **9**, *all involving proximate radical pairs*, contrast strongly to those observed for the *nonproximate* 1-phenylethyl radical-pair generated by thermolysis (105 °C) in benzene of *meso* and *S*,*S*-(−)-azobis-*sym*-1-phenylethane (k_{comb}/k_{rot} = 0.07)[29] and the likewise nonproximate pair from (*S*)-Ph_2-CHN=NCHMePh at 110 °C in benzene (k_{comb}/k_{rot} = 0.06).[30] In both of these nonproximate, singlet radical-pair systems, approximately 70% of the radicals diffuse from the initial solvent cage (30% cage reaction). The reduction in relative k_{comb} resulting from the presence of the intervening nitrogen molecule is strongly evident. It is also seen in value for k_{diff}/k_{comb} of 2.5 obtained for the azobis-*sym*-1-phenylethane system.[29]

Were the product accountabilities for the photorearrangements of **7** and **9** higher, values for k_{rot}/k_{diff} and k_{comb}/k_{diff} could be calculated. Reasonable values would result only if it were assumed that the yields of dimer **11** represent the total amount of noncage product formed with the remaining products, perhaps 95%, resulting from reaction within the solvent cage. A high degree of combination relative to rotation is observed for pair [**3**,**14**] from phosphite **7** (k_{comb}/k_{rot} = 11, avg) and **9** (k_{comb}/k_{rot} = 17, avg). Therefore, k_{comb}/k_{diff} values much larger than those seen for the proximate radical pairs formed from the $Ph_2C{=}C{=}NCHPhMe$[8] and the nitrogen-separated pairs from azobis-*sym*-1-phenylethane[29] would be anticipated.

In summary, the results of product studies, effects of added scavengers, the failure to detect ^{31}P CIDNP and CIDEP phenomena,[6,7,31] the stereochemical studies reported here, and comparisons to related research on proximate radical pairs,[8] point to the formation on direct irradiation of arylmethyl and 1-arylethyl phosphites (including **7** and **9**) of *short-lived, singlet radical pairs, [**3**,**14**], that predominantly undergo rapid recombination within the initial solvent cage.* One cannot rule out an important concerted component of these photorearrangements that features total retention of configuration at migratory carbon. However, in the absence of evidence for a concerted component, the available results are best interpreted in terms of very short-lived radical pairs, [**3**,**14**] (Scheme 1). This conclusion is in accord with

(26) E.g., viscosity-dependent k_{rot} of caged radicals have been correlated by $\eta^{-0.75}$ (Koenig, T.; Owens, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 8484) and by $\eta^{-0.50}$ (Johnson, R. A.; Seltzer, S. *J. Am. Chem. Soc.* **1973**, *95*, 938).

(27) Values of η for CCl_4 at 25 °C (0.91 cp) and 50 °C (0.66 cp) are reported in Lide, D. R. *Handbook of Organic Solvents*; CRC Press: Boca Raton, 1995 from which an interpolated value at 35 °C of 0.81 cp can be obtained.

(28) Gatlik, I.; Rzadek, P.; Gescheidt, G.; G., R.; Hellrung, B.; Wirz, J.; Dietliker, K.; Hug, G.; Kunz, M.; Wolf, J.-P. *J. Am. Chem. Soc.* **1999**, *121*, 8332−8336.

(29) Greene, F. D.; Berwick, M. A.; Stowell, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 867−874.

(30) Kopecky, K. R.; Gillan, T. *Can. J. Chem.* **1969**, *47*, 2371−2386.

(31) Sluggett, G. W.; Landis, M. S.; Turro, N. J. Unpublished results.

previous studies of photo-Arbuzov rearrangements of closely related 1-arylmethyl phosphites (**1**)[1,2,6,7,9,10,24]

Direct Irradiation of Optically Active Phosphite 8. It has been shown that introduction of the *p*-acetyl substituent in **1** (Ar = *p*-$MeCOC_6H_4$) results on direct irradiation in generation of triplet radical pairs.[3,6,7] The potential fates of the analogous triplet radical pairs [**3**,**14**] from direct irradiation of (*S*)-**8** are shown in Scheme 2. Since triplet radical pairs are likely to be relatively long-lived, the rotation step (k_{rot}) is expected to compete readily with k_{comb} and k_{diff} and be reversible as shown. Yields of products formed in the initial cage should be quite low as confirmed by the results seen in Tables 2 and 5. Large amounts of diffusion (k_{diff}, Scheme 2) yield the product of dimerization of cage-free 1-arylethyl radicals, **11b**, in 20% yield that accounts for 40% of the *p*-acetyl-1-phenylethyl radicals potentially formed.

The major portion of phosphonate **12** found (20% yield) most likely results from random couplings of cage-free radicals **3** and **14**. Thus, by comparison, the photorearrangement of the closely related dimethyl *p*-acetylbenzyl phosphite (**1**, Ar = *p*-MeC_6H_4) in the absence of trapping agents gives the phosphonate in 12% yield. However, under optimal scavenging by added benzyl bromine or thiophenol, only 3−5% of the phosphonate is formed, presumably from combination of the radical pair analogous to [**3**,**14**] prior to diffusion from the solvent cage.[3]

If phosphite **8** also gives a 3−5% yield of cage-formed phosphonate (**12**), the very small degree of retention (4% net retention, Table 5) at the migratory carbon observed on direct irradiation of (*S*)-**8** is expected (Scheme 2). Phosphonate **12** from random recombination will be totally racemic, and the initial triplet pairs (3−5%) that undergo combination in the solvent cage also should undergo considerable stereorandomization prior to intersystem crossing and coupling.

Stereochemical data in Table 5, derived by method I, show a roughly 4% net retention for phosphite **8** in line with the observed k_{comb}/k_{rot} ratio of 0.1, a minimum value. This ratio is derived from phosphonate formed predominantly outside the solvent cage following complete randomization of stereochemistry at the stereogenic carbon. Were phosphonate formed strictly within the solvent cage, the ratio of enantiomers would be higher than was observed and lead to a larger value for the ratio k_{comb}/k_{rot}. Nonetheless, the inverse ratio, k_{rot}/k_{comb}, will be assuredly be considerably higher than that for radicals from phosphite **7** under TEMPO scavenged conditions (11, avg value, Table 5).

Triplet-Sensitized Reactions of Phosphite 9. Relatively high yields of dimer **11c** (ca. 40% accountability of radicals **14** potentially formed), comparatively low yields of phosphonate **13** (20%), and the very small degree of retention of a configuration (% retention ≈ 2) observed on triphenylene-sensitized reactions of **9** (Table 3) are in line with the product distribution and stereochemical outcome obtained on direct irradiation of phosphite **8**, which was designed to give product from the triplet manifold upon excitation of the carbonyl functionality. Similarly, the triplet thioxanthone-sensitized reaction of dimethyl 1-naphthyl phosphite, **1** (Ar = 1-naphthyl), gives a 3−4% cage yield of the corresponding phosphonate.[24] The mechanism of triphenylene-sensitized rearrangement of *R*-**9** could be represented by a reaction scheme involving generation of triplet radical pairs that is completely analogous to Scheme 2 for direct irradiation of (*R*)-**8**. Thus, the stereochemical outcome from both the direct irradiation of (*R*)-**8** and triplet-sensitization of (*R*)-**9** *is diagnostic of the initial formation of triplet free radical pairs.*

Conclusions

For 1-arylethyl phosphites **7** and **9**, the proposed intermediacy of *short-lived singlet radical pairs* in the formation of 1-arylethylphosphonates **10** and **12** on direct UV irradiation is consistent with the relatively high yields of phosphonates formed and with the very high degree of stereospecificity (retention) observed at the stereogenic migratory carbon. Nonetheless, the partial loss of stereochemistry is *discordant with the operation of a purely concerted process*. The degree of retention of configuration at carbon is higher than that reported for the combination of other *proximate* singlet radical pairs in solution. Thus, the ratio $k_{comb}/k_{rot} = 11$ (avg, TEMPO-scavenged reaction, cyclohexane) determined for the proximate radical pairs [**3**,**14**], generated photochemically from phosphite (*S*)-**7**, is significantly higher than that reported for the thermally generated singlet radical pairs from ketenimine $Ph_2C{=}C{=}NCHPhMe$, for which k_{comb}/k_{rot} = 1.3 (acetonitrile) and 2.5 (CCl_4) even when the higher temperature of the ketenimine system is considered. This may be interpreted as consistent with a severalfold increase in k_{comb} for the radical pair from phosphite **7**, presuming that k_{rot} for the 1-phenylethyl radical, adjusted for the difference in reaction temperatures, is nearly the same for the two pairs. By contrast, the direct irradiation of phosphite **8** and sensitized photoreaction of phosphite **9** evidently generates primarily triplet radical pair intermediates and gives close to total stereorandomization at the stereogenic carbon in the product phosphonates formed by a combination of cage and noncage radical combination processes. The contrast in observed stereochemistry among the phosphites **7**−**9** is totally consistent with the outcome of product distribution studies[1−3,9,24] as well as CIDNP[6,31] and CIDEP[7,31] results for **7**−**9** and closely related phosphites. Thus, the stereochemical approach provides a *useful test* for the generation of predominantly singlet versus largely triplet radical pair populations in these photo-Arbuzov reaction systems.

Experimental Section

General Procedures and Materials. Air-sensitive materials were transferred by syringe or cannula or in a glovebag under an argon atmosphere. Spectrophotometric grade solvents were used as received unless otherwise noted. Diethyl ether, toluene, and tetrahydrofuran were dried over sodium/benzophenone and freshly distilled prior to use. Chemicals purchased from Aldrich Chemical Co. were (±)-1-phenylethanol, *(R)*-(+)-1-phenylethanol, (±)-α-methyl-1-naphthalene methanol, (−)-diisopinocampheylchloroborane, (−)-menthyl chloroformate. Tri-*n*-propyl phosphate was obtained from Lancaster Synthesis. Unless otherwise stated, distillations were performed with a short path apparatus. Flash chromatography was conducted on silica gel 60, 230−400 mesh, obtained from EM Science with the solvent system indicated. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Spectroscopic and Physical Data. Melting points are uncorrected. *J* values given in the ^1H NMR spectral data refer to proton−proton coupling unless otherwise stated. Ultraviolet (UV) spectra were obtained in acetonitrile and cyclohexane on a diode array spectrophotometer. Wavelength maxima (λ_{max}) are reported in nm with extinction coefficients, ϵ, in $M^{-1}\,cm^{-1}$.

Qualitative and quantitative gas chromatographic analyses were determined with a flame ionization detector (FID) and a DB-1 capillary column(1% methyl silicone) (10 or 30 m × 0.25 mm × 0.25 mm) with tri-*n*-propyl phosphate as internal standard. LR and HRMS were performed in the EI or the CI mode (70 eV). GC/MS spectra were taken in the EI or the CI mode. The column used was a 15 or 30 m × 0.25 mm × 0.25 mm DB-1 capillary column.

General Procedure for Determination of Enantiomeric Composition of Chiral Compounds. Column chromatographic purification (silica gel, chloroform) was done on all mixtures before separation on HPLC. The prepurified mixture was dissolved in 1−2 mL of the intended HPLC eluent solvent system. The solution was filtered through a Millex-HV_{13} (0.45 μm, 13 mm diameter) filter unit. The commonly used solvent system for the separation of phosphates and phosphonates from the mixture was 1.3−1.7% methanol in chloroform. HPLC separations were obtained under isocratic conditions (UV detector, 4.6 mm i.d. analytical, 10 mm i.d. semipreparative, or 21.4 mm i.d. preparative Dynamax HPLC column (100 A° spherical Microsorb packings in 5 μm particle size). Optimum flow rates were 10−16 mL/min on the 21.4 mm i.d. column.

Chiral high performance liquid chromatographic analyses were performed on a CHIRALCEL OD HPLC column (250 mm × 4.6 mm i.d.), equipped with a 50 mm × 4.6 mm i.d. guard column. Mobile phases were 95:5 to 90:10 of hexanes:2-propanol, optimal flow rate 1.0 mL/min.

Oxidation of Phosphites 7 and 9. A dilute solution of the starting phosphite in acetonitrile was treated with a 3.0 M solution of *tert*-butyl hydroperoxide in 2,2,4-trimethylpentane (small excess) in an ice bath. The solution was stirred for 10 min, and the solvent was removed by rotary evaporation. The mixture was purified by HPLC and subsequently analyzed for enantiomeric purity as described above. The unreacted starting material from each photolytic mixture was oxidized in the same manner, purified, and analyzed by chiral HPLC.

Quantum Yield Determinations. The procedure was previously described.[7]

General Procedure for Direct Irradiation of Phosphites 7−9. All sample preparation was carried out in a glovebag under an argon atmosphere. All solvent used is argon saturated. A 0.01 M solution of phosphite was prepared containing an equimolar amount of tri-*n*-propyl phosphate as internal standard in a 10 mL volumetric flask and transferred to a series of argon flushed quartz (phosphite **7**) or Pyrex (phosphite **8** and **9**) tubes (70 mm × 12 mm o.d.). The tubes were rubber septum capped, wrapped with Parafilm, that was tightened with copper wired, and further wrapped with a piece of aluminum foil. The solution was purged with (5 min) and then irradiated in a Rayonet photochemical apparatus equipped with 6 × 253.7 nm lamps (phosphite **7**) or 6 × 300 nm lamps (phosphite **9**). Solutions of **8** were irradiated using light from a 450 W medium-pressure Hg lamp filtered through a uranium glass sleeve. The reactions were monitored by GC analysis (duplicate or triplicate injections, results averaged).

Triphenylene-Sensitized Photoreaction of 9. Similarly, under an argon atmosphere, a 10 mL 0.01 M acetonitrile solution of **9** containing an equimolar amount of tri-*n*-propyl phosphate internal standard and 2 equiv of triphenylene was partitioned between three Pyrex tubes fixed to 10/30 joints, degassed with four freeze−pump−thaw cycles (0.01 mmHg), and flame-sealed under vacuum. The samples were irradiated with light from a medium pressure 450-W Hg lamp and filtered through a uranium glass filter sleeve. Product yields were determined by GC after 7, 27, and 60 h after oxidation with *tert*-butyl hydroperoxide in 2,4,6-trimethylpentane. The oxidized unreacted **9** and the phosphonate **13** were isolated by HPLC, and the stereochemistry of enantiomeric compositions of both components were determined as described earlier.

Preparation of 2-(1-Phenylethyloxy)-1,3,2-dioxaphosphorinane (7). At room temperature under argon atmosphere, a solution of 1-phenylethanol (3.0 g, 25 mmol) in 10 mL of acetonitrile was added dropwise to a solution of *N*,*N*-diethyl-1,3,2-dioxaphosphorinan-2-amine (4.4 g, 25 mmol) and 1-*H*-tetrazole (18 mg, 2.5 mmol) in 20 mL of acetonitrile. The solution was stirred at room temperature for an additional 1 h. The solvent was removed in vacuo. A 15 mL portion of 1:1 diethyl ether:ethyl acetate was added to the residue. The solution was filtered by Schlenk techniques under argon. Solvent removal in vacuo and vacuum distillation gave **7** (3.5 g, 5.0 mmol, 62% yield) as a colorless liquid: bp 80−82 °C (0.05 mmHg) (99% purity by GC). ^{31}P NMR (121 MHZ, $CDCl_3$, {^{1}H}) δ 130.09; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44−1.52 (m, 1 H), 1.59 (d, 3 H, $^3J_{HP}$ = 6.6 Hz), 2.32−2.48 (m, 1 H), 3.60−3.70 (m, 1 H), 3.74−3.84 (m, 1 H), 4.23−4.33 (m, 1 H), 4.49−4.58 (m, 1 H), 5.16 (dq, 1 H, $^3J_{HP}$ = 8.7 Hz, ^3J = 6.5 Hz), 7.22−7.42 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$, {^{1}H}) δ 25.24 (d, $^3J_{CP}$ = 3.7 Hz), 28.68 (d, $^3J_{CP}$ = 5.3 Hz), 59.28 (d, $^2J_{CP}$ = 2.3 Hz), 59.32 (d, $^2J_{CP}$ = 2.4 Hz), 71.69 (d, $^2J_{CP}$ = 20.3 Hz), 126.02, 127.63, 128.61, 144.51 (d, $^3J_{CP}$ = 3.2 Hz); UV (CH_3CN): 248 (ϵ 183), 254 (ϵ 210), 258 (ϵ 227), 264 (ϵ 184); GC-EIMS (70 eV) *m*/*z* (rel intensity) 226 $[M]^+$ (6), 122 (29), 105 $[CHCH_3Ph]^+$ (100), 77 $[Ph]^+$ (24); HRMS (EI) *m*/*z* $[M]^+$ calcd for $C_{11}H_{15}O_3P$: 226.0757, found: 226.0747.

Preparation of (*R*)-2-(1-Phenylethyloxy)-1,3,2-dioxaphosphorinane ((*R*)-7). By the procedure racemic **7**, reaction of *N*,*N*-diethyl-1,3,2-dioxaphosphorinan-2-amine (1.3 g, 7.4 mmol), (*R*)-(+)-1-phenylethanol (0.9 g, 7.4 mmol) (97/3 *R*/*S* by HPLC on a CHIRALCEL OD), and 1-*H*-tetrazole (7.0 mg, 1 mmol) gave 1.1 g (4.9 mmol, 66% yield) of (*R*)-**7** (98.8% purity by GC, 97/3 *R*/*S* ratiodetermined on the phosphate).

Preparation of 2-(1-Phenylethyloxy)-2-oxo-1,3,2-dioxaphosphorinane (7-O). Oxidation of racemic **7** (0.9 g, 4.1 mmol) by *tert*-butyl hydroperoxide (1.4 mL), as described earlier, gave, after HPLC purification, 1.0 g of its oxide as an oil (4.0 mmol, 97% yield, 99.8% purity by GC). ^{31}P NMR (121 MHz, $CDCl_3$, {^{1}H}) δ −7.50; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.62−1.64 (m, 1 H), 1.68 (d, ^3J = 6.6 Hz), 2.10−2.26 (m, 1 H), 3.95−4.05 (m, 1 H), 4.11−4.24 (m, 1 H), 4.32−4.39 (m, 2 H), 5.53 (dq, 1 H, $^3J_{HP}$ = 7.6 Hz, ^3J = 6.5 Hz), 7.29−7.43 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$, {^{1}H}) δ 23.71 (d, $CHCH_3$, $^2J_{CP}$ = 4.7 Hz), 25.59 (d, $^3J_{CP}$ = 6.7 Hz), 68.09 (d, $^2J_{CP}$ = 6.8 Hz), 68.61 (d, $^2J_{CP}$ = 6.7 Hz), 76.23 (d, J_{CP} = 5.2 Hz), 125.57, 128.06, 128.33, 141.05 (d, $^3J_{CP}$ = 5.7 Hz); GC-EIMS (70 eV) *m*/*z* (rel intensity) 242 $[M]^+$, 139 (61), 121 $[(OCH_2CH_2CH_2O)P{=}O]^+$ (10), 105 $[CHCH_3Ph]^+$ (52), 104 (100), 77 $[Ph]^+$ (33); HRMS (EI) *m*/*z* $[M]^+$ calcd for $C_{11}H_{15}O_4P$: 242.0708, found: 242.0726. Anal. Calcd for $C_{11}H_{15}O_4P$: C, 54.55; H, 6.24. Found: C, 54.62; H, 6.20.

2-(1-Phenylethyl)-2-oxo-1,3,2-dioxaphosphorinane (10) was isolated by HPLC (1.1% methyl alcohol in chloroform) from the products of photolysis of dioxaphosphorinane **7** as a white solid. Recrystallization from ether/pentane gave colorless needles (mp 90−91 °C). ^{31}P NMR (121 MHz $CDCl_3$, {^{1}H}) δ 0.99; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.64 (dd, $^3J_{HP}$ = 18.7 Hz, ^3J = 7.5 Hz), 1.67−1.79 (m, 1 H), 1.81−1.92 (m, 1 H), 3.31 (dq, 1 H, $^3J_{HP}$ = 22.2 Hz, ^3J = 7.4 Hz), 3.95−4.14 (m, 2 H), 4.38−4.48 (m, 2 H), 7.25−7.36 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$, {^{1}H}) δ 15.03 (d, $^2J_{CP}$ = 6.7 Hz), 26.21 (d, $^3J_{CP}$ = 6.7 Hz), 38.05 (d, $^1J_{CP}$ = 134.9 Hz), 66.21 (d, $^2J_{CP}$ = 2.7 Hz), 66.31 (d, $^2J_{CP}$ = 2.7 Hz), 127.21 (d, J_{CP} = 3.5 Hz), 128.51, 128.55 (d, J_{CP} = 1.6 Hz), 128.65, 137.52 (d, $^3J_{CP}$ = 7.5 Hz); UV (CH_3CN): 242 (ϵ 147), 250 (ϵ 193), 258 (ϵ 236), 264 (ϵ 168), 268 (ϵ 94); GC-EIMS (70 eV) *m*/*z* (relative intensity) 226 $[M]^+$ (25), 105 $[CHCH_3Ph]^+$ (100), 77 $[Ph]^+$ (23); Anal. Calcd for $C_{11}H_{15}O_3P$: C, 58.41; H, 6.68. Found: C, 58.08; H, 6.37.

Preparation of (*S*)-1-(4-(1-Hydroxyethyl)phenyl)ethanone. The procedure of Brown et al. was followed with a slight modification.[32−34] A reduction of 2-(4-acetylphenyl)-2-methyl-1,3-dioxolane (see Supporting Information, 0.61 g, 2.9 mmol) with diisopinocampheylchloroborane ((−)-DIP chloride) (1.1 g, 3.3 mmol) followed by a treatment with acetaldehyde (0.15 g,

(32) Brown, H. C.; Chandrasekharan, J.; Ramachandran, P. V. *J. Am. Chem. Soc.* **1988**, *110*, 1539−1546.

(33) Brown, H. C.; Ramachandran, P. V.; Teodorovic, A. V.; Rangaishenvi, M. V. *J. Org. Chem.* **1992**, *57*, 2379−2386.

(34) Brown, H. C.; Ramachandran, P. V. *Acc. Chem. Res.* **1992**, *25*, 16−24.

3.5 mmol) gave the alcohol (0.33 g, 2.0 mmol, 70%) as a colorless thick oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.54 (d, 3 H, J = 6.4 Hz), 2.58 (s, 3 H), 4.96 (q, 1 H, J = 5.6 Hz), 7.45 (d, 2 H, J = 8.5 Hz), 7.92 (d, 2 H, J = 8.3 Hz) (lit.[35]); ^{13}C NMR (75 MHz, $CDCl_3$, {^{1}H}) δ 25.27, 26.58, 69.77, 125.41, 128.56, 136.07, 151.24, 197.98 (s, O=CCH_3) (lit.[35]). The optical purity of the alcohol was determined after its conversion to the corresponding diastereomeric carbonates following the method of Westley and Halpern employing (−)-menthyl chloroformate.[36] The enantiomeric ratio (R/S) was 97.5/2.5 (GC).

Preparation of 2-(1-(4-Acetylphenyl)ethyloxy)-1,3,2 dioxaphosphorinane (8). The reaction of *N*,*N*-diethyl-1,3,2-dioxaphosphorinan-2-amine (1.3 g, 7.3 mmol), 1-(4-acetylphenyl)-ethanol (1.2 g, 7.2 mmol), and 1-*H*-tetrazole (7.0 mg, 1.0 mmol) using the method to prepare phosphite **7** afforded **8** (99% purity by GC) as a pale yellow thick oil (1.2 g, 4.4 mmol, 62%) after flash chromatography purification. ^{31}P NMR (121 MHz, $CDCl_3$, {^{1}H}) δ 129.33; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.61 (d, 3 H, ^3J = 6.4 Hz), 1.67−1.79 (m, 1 H), 2.43 (m, 1 H), 2.60 (d, 3 H,^3J = 0.7 Hz), 3.65−3.75 (m, 1 H), 3.78−3.88 (m, 1 H), 4.27−4.37 (m, 1 H), 4.50−4.60 (m, 1 H), 5.22 (dq, 1 H, J = 8.7, 6.6 Hz), 7.51 (d, 2 H, J = 8.3 Hz), 7.96 (d, 2 H, J = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, {^{1}H}) δ 24.90 (d, $^3J_{CP}$ = 3.6 Hz), 26.51, 28.30 (d, $^3J_{CP}$ = 5.2 Hz), 59.35 (d, $^2J_{CP}$ = 1.0 Hz), 59.44 (d, $^2J_{CP}$ = 1.6 Hz), 70.89 (d, $^2J_{CP}$ = 20.2 Hz), 125.70, 128.45, 136.16, 149.07 (d, J_{CP} = 3.1 Hz), 197.60 (s); UV (CH_3CN): 278 (ϵ 1350), 284 (ϵ 340), 288 (ϵ 690), 314 (ϵ 130); GC-EIMS (70 eV) *m*/*z* (relative intensity) 268 $[M]^+$ (100), 253 $[M - CH_3]^+$ (22), 227 (84), 225 $[M - O{=}CCH_3]^+$ (11), 43 $[O{=}CCH_3]^+$ (36); HRMS $[M]^+$ calcd for $C_{13}H_{17}O_4P$: 268.0864, found: 268.0870.

Preparation of (*S*)-2-(1-(4-Acetylphenyl)ethyloxy)-1,3,2-dioxaphosphorinane ((*S*)-8). The compound was prepared from the reaction of (*S*)-1-(4-acetylphenyl)ethanol (0.10 g, 0.61 mmol), *N*,*N*-diethyl-1,3,2-dioxaphosphorinan-2-amine (0.11 g, 0.62 mmol), and 1-*H*-tetrazole (0.7 mg, 0.1 mmol). Pure **8** (98.7% purity by GC) was obtained after flash chromatography (0.11 g, 0.40 mmol, 65%).

Preparation of 2-(1-(4-Acetylphenyl)ethyloxy)-2-oxo-1,3,2-dioxaphosphorinane (8-O). Compound **8** (1.4 g, 5.2 mmol) was oxidized with *tert*-butyl hydroperoxide (1.0 mL) as described earlier. HPLC purification yielded a colorless thick oil (1.2 g, 4.4 mmol, 62%). ^{31}P NMR (121 MHz, $CDCl_3$, {^{1}H}) δ 129.33; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.57 (d, 3 H, ^3J = 6.4 Hz), 1.62−1.75 (m, 1 H), 2.40 (m, 1 H), 2.51 (d, 3 H, ^3J = 0.7 Hz), 3.60−3.70 (m, 1 H), 3.71−3.82 (m, 1 H), 4.21−4.31 (m, 1 H), 4.40−4.50 (m, 1 H), 5.34 (dq, 1 H, J = 8.7, 6.6 Hz), 7.51 (d, 2 H, J = 8.3 Hz), 7.96 (d, 2 H, J = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, {^{1}H}) δ 25.70 (d, $^3J_{CP}$ = 4.0 Hz), 25.51, 29.30 (d, $^3J_{CP}$ = 5.2 Hz), 59.54 (d, $^2J_{CP}$ = 1.0 Hz), 59.64 (d, $^2J_{CP}$ = 1.6 Hz), 69.74 (d, $^2J_{CP}$ = 20.2 Hz), 126.50, 128.35, 134.15, 148.12 (d, J_{CP} = 3.1 Hz), 198.60 (s); UV (CH_3CN): 282 (ϵ 1438), 288 (ϵ 948), 292 (ϵ 750), 318 (ϵ 160); GC-EIMS (70 eV) *m*/*z* (relative intensity) 284 $[M]^+$ (100), 253 $[M - CH_3]^+$ (50), 225 $[M - O{=}CCH_3]^+$ (23), 43 $[O{=}CCH_3]^+$ (25). Anal. Calcd for $C_{13}H_{17}O_5P$: C, 54.93; H, 6.03. Found: C, 54.87; H, 6.00.

2-(1-(4-Acetylphenyl)ethyl)-2-oxo-1,3,2 dioxaphosphorinane (12). The title compound was isolated following photolysis of **8** on HPLC (1.5% methanol in chloroform). Recrystallization from ether/pentane yielded **12** as white needles: mp 100−101 °C. ^{31}P NMR (121 MHz, $CDCl_3$, {^{1}H}) δ 24.34; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.65 (dd, 3H, $^3J_{HP}$ = 18.4, ^3J = 7.5 Hz), 1.87 (m, 2 H), 2.60 (s, 3 H), 3.38 (dq, 1 H, $^2J_{HP}$ = 22.5, ^3J = 7.4 Hz), 4.12 (m, 2 H), 4.46 (m, 2 H), 7.46 (m, 2 H), 7.94 (d, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, {^{1}H}) δ 14.86 (d, $^2J_{CP}$ = 5.2 Hz), 26.1 (d, $^3J_{CP}$ = 7.8 Hz), 26.51, 37.88 (d, $^1J_{CP}$ = 135.4 Hz), 66.19 (d, $^2J_{CP}$ = 7.3 Hz), 128.42 (d, J_{CP} = 2.6 Hz), 128.72 (d, J_{CP} = 6.2 Hz), 135.88 (d, J_{CP} = 3.6 Hz), 143.00 (d, J_{CP} = 7.3 Hz), 197.60 (s); UV (CH_3CN): 280 (ϵ 1428), 286 (ϵ 938), 290 (ϵ 740), 316 (ϵ 150); GC-EIMS (70 eV) *m*/*z* (relative intensity) 268 $[M]^+$ (49), 254 (14), 253 $[M - CH_3]^+$ (100), 147 (77), 77 $[Ph]^+$ (14), 43 $[O{=}CCH_3]^+$ (61). Anal. Calcd for $C_{13}H_{17}O_4P$: C, 58.21; H, 6.39. Found: C, 58.19; H, 6.39.

Preparation of Dimethyl 1-(1-Naphthyl)ethyl Phosphite (9). This compound was prepared from the reaction of dimethyl *N*,*N*-diethylphosphoramidite (5.3 g, 32 mmol), α-methyl-1-naphthalene methanol (4.3 g, 25 mmol), and 1-*H*-tetrazole (280 mg, 4.0 mmol) following the procedure for preparation of **7**. Pure **9** (98.5% by GC) was purified by flash chromatography as a colorless oil (4.5 g, 17 mmol, 67%). ^{31}P NMR (121 MHz, $CDCl_3$, {^{1}H}) δ 132.07; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.71 (d, 3 H, ^3J = 6.6 Hz), 3.41 (d, 3 H, $^3J_{HP}$ = 10.9 Hz), 3.44 (d, 3 H, $^3J_{HP}$ = 10.5 Hz), 6.06 (dq, 1 H, $^3J_{HP}$ = 8.8 Hz, ^3J = 6.4 Hz), 7.40−7.50 (m, 3 H), 7.69 (d, 1 H, J = 7.1 Hz), 7.73 (d, 1 H, J = 8.1 Hz), 7.82 (d, 1 H, J = 7.6 Hz), 8.10 (d, 1 H, J = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, {^{1}H}) δ 24.87 (d, $^3J_{CP}$ = 3.1 Hz), 48.82 (d, $^2J_{CP}$ = 9.3 Hz), 49.06 (d, $^2J_{CP}$ = 9.9 Hz), 68.57 (d, $^2J_{CP}$ = 15.0 Hz), 123.05, 123.07, 125.33, 125.85, 127.84, 128.75, 129.70, 133.62, 139.46, 139.51; UV (CH_3CN): 264 (ϵ 3.7 × 10^4), 274 (ϵ 6.0 × 10^4), 284 (ϵ 7.1 × 10^4), 294 (ϵ 4.8 × 10^4); GC-EIMS (70 eV) *m*/*z* (relative intensity) 264 $[M]^+$ (8), 155 $[CHCH_3C_{10}H_7]^+$ (100), 154 (45), 127 $[C_{10}H_7]^+$ (15); HRMS $[M]^+$ calcd for $C_{14}H_{17}O_3P$: 264.0915, found: 264.0913.

Preparation of Dimethyl 1-(1-Naphthyl)ethyl Phosphate (9-O). The oxidation of **9** (0.9 g, 3.4 mmol) using *tert*-butyl hydroperoxide followed by HPLC purification (1% methyl alcohol in chloroform) resulted in (0.9 g, 3.3 mmol, 96%) of the oxide as a colorless oil. ^{31}P NMR (121 MHz, $CDCl_3$, {^{1}H}) δ 1.09; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.82 (d, 3 H ^3J = 6.6 Hz), 3.58 (d, 3 H, $^3J_{HP}$ = 11.2 Hz), 3.73 (d, 3 H, $^3J_{HP}$ = 11.0 Hz), 6.25 (dq, 1 H, $^2J_{HP}$ = 6.9 Hz, ^3J = 6.9 Hz), 7.46−7.57 (m, 3 H), 7.66 (d, 1 H, J = 6.6 Hz), 7.80−7.89 (m, 2 H), 8.12 (d, 1 H, J = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, {^{1}H}) δ 23.84 (d, $^3J_{CP}$ = 4.2 Hz), 54.11 (d, $^2J_{CP}$ = 6.2 Hz), 74.44 (d, $^2J_{CP}$ = 5.7 Hz), 122.98, 123.14, 125.28, 125.65, 126.29, 128.62, 128.85, 129.68, 133.69, 137.17 (d, J_{CP} = 5.2 Hz); UV (CH_3CN): 262 (ϵ 3.7 × 10^4), 272 (ϵ 6.0 × 10^4), 282 (ϵ 7.0 × 10^4), 292 (ϵ 4.8 × 10^4); GC-EIMS (70 eV) *m*/*z* (relative intensity) 280 $[M]^+$ (14), 155 $[CHCH_3C_{10}H_7]^+$ (41), 154 (95), 153 (100), 127 $[C_{10}H_7]^+$ (45); HRMS (EI) *m*/*z* $[M]^+$ calcd for $C_{14}H_{17}O_4P$: 280.0865, found: 280.0879. Anal. Calcd for $C_{14}H_{17}O_4P$: C, 60.00; H, 6.11. Found: C, 60.10; H, 6.15.

Dimethyl 1-(1-naphthyl)ethylphosphonate (13) was isolated from the products of photolysis of 1-(1-naphthyl)ethyl dimethyl phosphite (**9**) by HPLC (1.5% methanol in chloroform). ^{31}P NMR (121 MHz, $CDCl_3$, {^{1}H}) δ 32.82; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.70 (dd, $CHCH_3$, $^3J_{HP}$ = 18.3 Hz, 3J = 7.3 Hz), 3.34 (d, 3 H, $^3J_{HP}$ = 10.5 Hz), 3.68 (d, 3 H, $^3J_{HP}$ = 10.5 Hz), 4.11 (dq, 1 H, $^2J_{HP}$ = 23.2 Hz, $^3J_{HH}$ = 7.5 Hz), 7.43−7.55 (m, 3 H), 7.70−7.85 (m, 3 H), 8.08 (d, 1 H, J = 8.6); ^{13}C NMR (75 MHz, $CDCl_3$, {^{1}H}) δ 16.20 (d, $^2J_{CP}$ = 5.2 Hz), 31.81 (d, $^1J_{CP}$ = 139.0 Hz), 52.58 (d, $^2J_{CP}$ = 7.3), 53.07 (d, $^2J_{CP}$ = 7.4), 122.75, 125.30 (d, J_{CP} = 3.6 Hz), 125.39, 125.83 (d, J_{CP} = 6.7 Hz), 126.04, 127.50 (d, J_{CP} = 3.6 Hz), 128.78 (d, J_{CP} = 1.0 Hz), 131.32 (d, J_{CP} = 7.3 Hz), 133.65 (d, J_{CP} = 1.2 Hz), 133.73 (d, J_{CP} = 6.2 Hz); UV (CH_3CN): 264 (ϵ 3.9 × 10^4), 274 (ϵ 6.2 × 10^4), 284 (ϵ 7.3 × 10^4), 294 (ϵ 5.0 × 10^4); GC-EIMS (70 eV) *m*/*z* (relative intensity) 264 $[M]^+$ (15), 155 $[CHCH_3C_{10}H_7]^+$ (100); HRMS (EI) *m*/*z* $[M]^+$ calcd for $C_{14}H_{17}O_3P$: 264.0915, found: 264.0924. Anal. Calcd for $C_{14}H_{17}O_3P$: C, 63.63; H, 6.48. Found: C, 63.89; H, 6.52.

Acknowledgment. This research was supported by grants from the National Science Foundation and the National Institutes of Health.

Supporting Information Available: Experimental details and spectral data for preparations of precursor to phosphites **7**−**9**. Tables showing the configurational stabilities of unreacted phosphites **7** and **9** over the course of irradiation. This material is available free of charge via the Internet at http://pubs.acs.org.

JO001545E

(35) Baldwin, B. W.; Morrow, C. J. *Tetrahedron Asymmetry* **1996**, *7*, 2871−2878.

(36) Westley, J. W.; Halpern, B. *J. Org. Chem.* **1968**, *33*, 3978−3980.