Notes

Triplet-Sensitized Photorearrangements of Six-Membered-Ring 2-Phenylallyl Phosphites. Reaction Efficiency and Stereochemistry at Phosphorus

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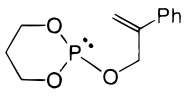
Introduction

2-Phenylallyl phosphites undergo triplet benzophenone- or triphenylene-sensitized photorearrangement to the corresponding phosphonates with the regiochemistry illustrated (deuterium label) by the acyclic example **1** → **2** (Scheme 1).[1] The overall process is energetically very favorable. Chemical yields with **1** are near-quantitative and accompanied by relatively high quantum yields for phosphonate formation, ϕ_P, of 0.2−0.3.[1b−d] Mechanistically, it has been proposed[1] that the relaxed (90°) $\pi-\pi^*$ triplet of **1** behaves as a 1,2-biradical, **3**, whose terminus mimics a primary monoradical and oxidatively adds to phosphorus to give phosphoranyl 1,3-biradical **4** (Scheme 1).[1d] β Scission of **4** provides the two π bonds in **2**. Strikingly, the quantum yields for **5** are reduced to 0.002−0.003.[1c,d] However, the *chemical* yields of phosphonate from **5** and its analogue **7** remain reasonably high. These photorearrangements have potential synthetic advantage over the classical Arbuzov reaction approach to phosphonates in that it avoids the use of allyl halides, such as CH_2=$CPhCH_2Br$, which may be accompanied by allylation at multiple nucleophilic sites. Allylphosphonates are readily converted to synthetically useful vinylphosphonates.[2]



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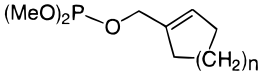
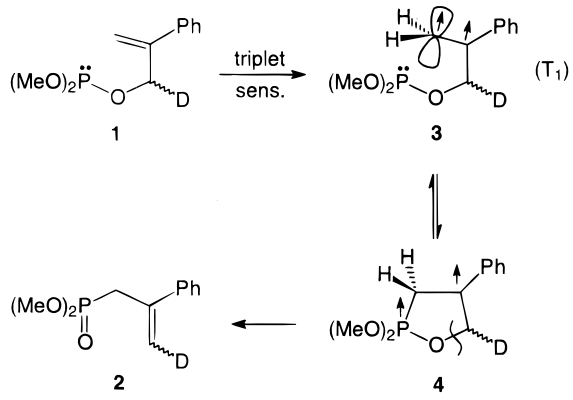


6 n = 1-3

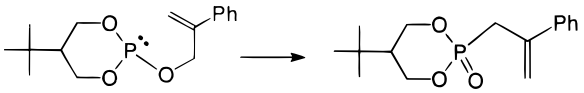
Allyl phosphites whose double bonds are not phenyl-substituted also undergo regiochemically analogous, triplet xylene-sensitized photorearrangements to allylphosphonates.[3] Relative quantum yields, ϕ_P, are strongly

Scheme 1



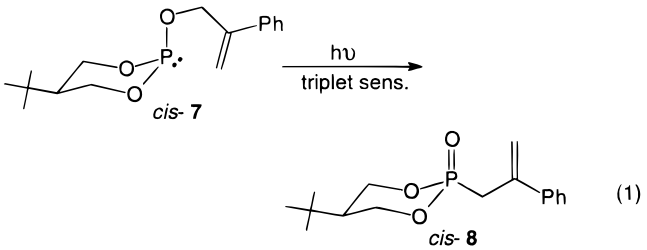
enhanced[3b] when the double bond is in a five-membered ring (**6**, $n = 1$) which likely imparts higher energy and a longer lifetime to the planar alkene $\pi-\pi^*$ triplet.[4]

We report here studies of the stereochemistry at phosphorus of the triphenylene triplet-sensitized photorearrangements of diastereomeric phosphites *cis*- and *trans*-**7**. Cis and trans refer to the relationship of the *tert*-butyl and 2-phenylallyloxy substituents on the 1,3,2-dioxaphosphorinane rings of **7**. The product *phosphonate* **8** is designated cis when the *tert*-butyl and phosphoryl oxygen (P=O) are attached cis to one another on the ring. The present assignment for **8** differs from previous practice[5] but follows the usual priority rules (O > C).



7 **8**

Indeed, we show that the photorearrangements of **7** proceed in good yields with nearly exclusive *retention* of configuration at phosphorus, i.e., *cis*-**7** → *cis*-**8** and *trans*-**7** → *trans*-**8** (eq 1). This new finding is in accord with the



cis- **7** *cis*- **8** (1)

operation of a mode 4 permutation **15** → **16** (Scheme 2),

(1) (a) Bentrude, W. G.; Lee, S.-G.; Akutagawa, K.; Ye, W.-Z.; Charbonnel, Y *J. Am. Chem. Soc.* **1987**, *109*, 1577. (b) Bentrude, W. G.; Wu, Y. W.; Ganapathy, W.; Baik. W.; Lee, S.-G.; Cambron, R. T.; Harris, J. M. *Phosphorus, Sulfur, Silicon* **1993**, *75*, 312. (c) Ganapathy, S.; Cambron, R. T.; Dockery K. P.; Wu, Y.-W.; Harris, J. M.; Bentrude, W. G. *Tetrahedron Lett.* **1993**, *34*, 5987. (d) Bentrude, W. G.; Dockery K. P.; Ganapathy, S.; Lee, S.-G.; Tabet, M.; Wu, Y.-W.; Cambron, R. T.; Harris, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 6192.

(2) Minami, T.; Motoyoshiya, J. *Synthesis* **1992**, 333.

(3) (a) Bentrude, W. G. Photorearrangements of Allyl Phosphites. In *Phosphorus Chemistry, Developments in American Science,* ACS Symposium Series 486, Walsh, E. N., Griffith, E. J., Parry, R. W., Quin, L. D., Eds.; American Chemical Society: Washington D. C., 1992; Ch. 11. (b) Huang, Y.; Bentrude, W. G. *Tetrahedron Lett.* **1997**, *38*, 6989.

(4) (a) Caldwell, R. A.; Zhou, L. *J. Am. Chem. Soc.* **1994**, *116*, 2271. (b) Unett, D. J.; Caldwell, R. A. *Res. Chem. Intermed.* **1995**, *21*, 665. (c) Unett, D. J.; Caldwell, R. A.; Hrncir, D. C. *J. Am. Chem. Soc.* **1996**, *118*, 1682.

(5) For a recent example, see: Bhanthumnavin, W.; Arif, A.; Bentrude, W. G. *J. Org. Chem.* **1998**, *63*, 7753. See also ref 6.

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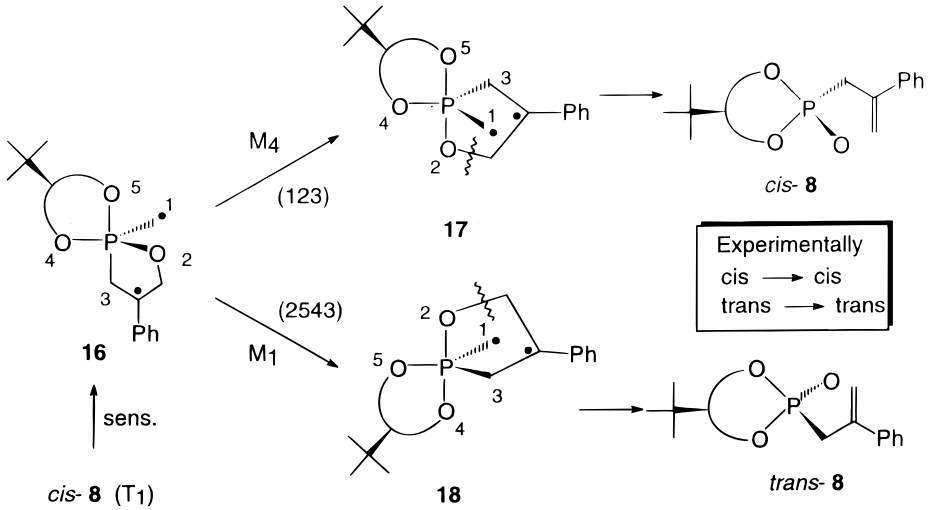
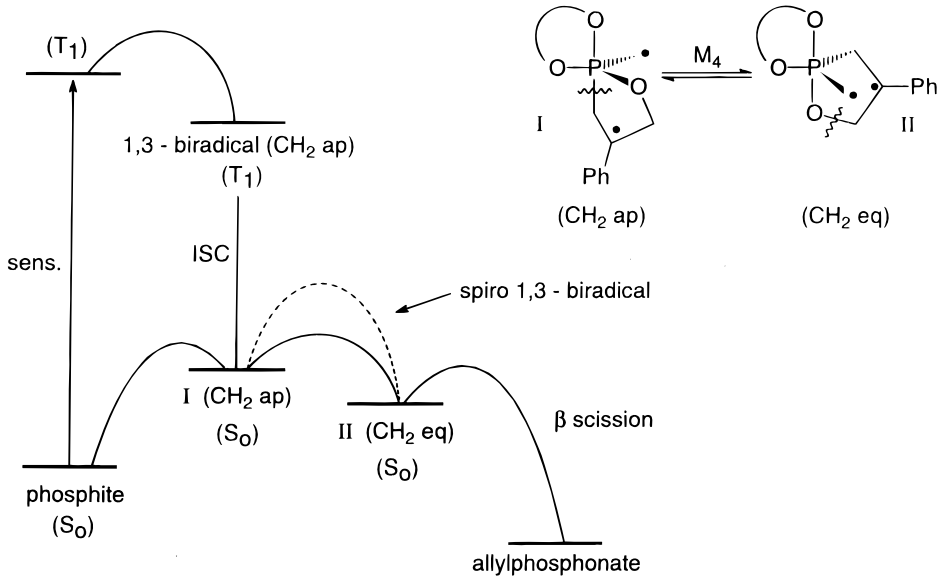
Scheme 2



Scheme 3



known from ESR studies[6] for cyclic *phosphoranyl monoradicals*. The retentive stereochemistry provides conclusive evidence against a mode 1 permutation (**16** → **18**, Scheme 2) that predominates for truly pentacovalent phosphorus species. Furthermore, Scheme 2 is totally consistent with arguments[1c,d] that explain the low quantum yield, ϕ_P, for phosphonate formation from **5**. Unfortunately, the synthetically interesting triplet triphenylene-sensitized photorearrangement of the nucleoside-based 2-phenylallyl phosphite **9** is found to produce only low yields of phosphonate **10**.

Cyclic phosphite **11** does not give phosphonates **12** or **13** on *m*-xylene triplet sensitization nor do the corresponding phosphonates arise from allyl and 2-methylallyl phosphites **14** and **15**. The findings for **11**, **14**, and **15**, along with those for **1**, **5**, **7**, and **9**, are discussed in terms of the energy diagram of Scheme 3 which unifies *for the first time* our understanding of the effects of allyl phosphite structure on the quantum efficiencies of these photorearrangements in terms of a 1,2-diradical $\pi-\pi^*$ model.[4]

Results and Discussion

Triplet-Sensitized Photorearrangement of *cis*- and *trans*-7. Phosphite **7** was prepared under conditions of kinetic control (trans/cis = 92/8) and then partially equilibrated thermally to give a second nonequilibrium ratio of diastereomers (trans/cis = 57/43). Thoroughly deoxygenated dilute solutions of phosphite **7**, containing triphenylene as triplet sensitizer, were irradiated in Pyrex tubes with light from the 350 nm lamps of a Rayonet reactor (Table 1).

The reaction was followed by GC (internal standard method) to assay the total consumption of the diastereomers of phosphite **7** (cis plus trans) and to quantitate the amount of each individual diastereomer of **8** formed. Consumption of the individual cis and trans diastereomers of **7**, interconverted on GC, had to be monitored

(6) Five-coordinate phosphorus modes of permutation have been defined (Musher, J. I. *J. Chem. Educ.* **1974**, *51*, 94). (a) Griller, D.; Roberts, B. P. *J. Chem. Soc, Perkin Trans. 2* **1973**, 1416. (b) Dennis, R. W.; Roberts, B. P. *J. Chem. Soc, Perkin Trans. 2* **1975**, 140. (c) Davies, A. G.; Parrott, M. J.; Roberts, B. P.; Skowronska, A. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1154. (d) Cooper, J. W.; Parrot, M. J.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1977**, 730. (e) Roberts, B. P.; Singh, K. *J. Chem. Soc., Chem. Commun.* **1979**, 980.

Table 1. Stereochemistry of Photorearrangement of 7[a]

time, h	cis/trans **7**	% conv of **7**[d]	% **8** formed[d]	cis/trans **7**[e] consump	cis/trans **8**[f] formed
0[b,f]	8/92	0	0		
24	8/92	32	90	8/92	8/92
72	9/91	61	80	9/93	10/90
0[c,f]	43/57	0	0	0	0
24	40/60	39	66	47/53	43/57
48	43/57	58	72	44/56	42/58
72	44/58	85	69	43/57	44/56

[a] By ^{31}P NMR vs internal standard (n-PrO)$_3$PO. [b] 0.86 mol of **7**, 0.009 M **7**. [c] 1.2 mol of **7** (0.012 M). [d] Total cis plus trans. [e] Based on moles of *cis*- and *trans*-**7** individually consumed. [f] Calculated from moles of individual cis and trans isomers of **8** formed. [f] Both reactions contained an approximate 0.6 equiv of triphenylene.

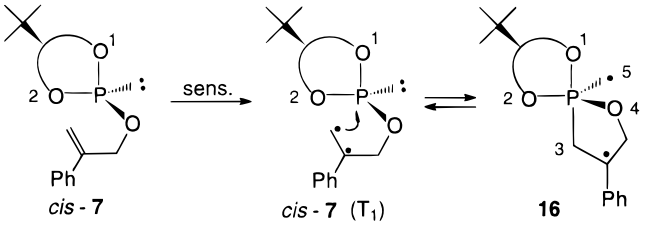
quantitatively, along with those for the diastereomers of **8**, by integration of their ^{31}P NMR signals against internal standard, (n-PrO)$_3$PO. Alternatively, essentially identical results were obtained if the product mixture was concentrated under argon and then oxidized by *tert*-BuOOH to convert remaining phosphite to phosphate which was quantitatively assayed by GC. This oxidation occurs near-quantitatively with retention of configuration at phosphorus.[7] The results in Table 1 were obtained by the ^{31}P NMR method. Photolysis in the absence of triphenylene gave no conversion of **7** to **8**.

Phosphonates **8** were isolated by chromatography and identified by comparison to authentic material prepared independently. The cis and trans identities of the individual diastereomers of **7** and **8** were readily assigned. (The ^{31}P shift of the diastereomer with the RO or R group positioned axially on phosphorus in its predominant conformer is invariably more upfield[8]).

Phosphonate yields in Table 1 are not quantitative but reasonably good. Workup of a 151-mg scale photoreaction gave a 54% total *isolated* yield of a mixture of the two diastereomers of **8** (99% conversion). The amounts of each individual diastereomer of **7** consumed are expressed in Table 1 as percentage ratios of the total amount of **7** consumed (cis/trans **7** consumed). Likewise, the accountability yields of each diastereomer of phosphonate **8** formed are given as percentage ratios. The cis/trans ratio of consumed phosphite is close to the cis/trans ratio of phosphonate formed in each case. Thus, the photorearrangement *proceeds with essentially complete retention of configuration at phosphorus.* This is clearly represented for *cis*-**7** → *cis*-**8** by eq 1. This conclusion, however, requires that two things be true of these reactions.

First, the diastereomers of **7** must be configurationally stable under the photoirradiation conditions. Indeed, the trans/cis ratio of phosphite **7** was unchanged in 96-h at room-temperature in the absence of UV light. Furthermore, photoreactions on solutions rich in the kinetically preferred *trans*-**7** (cis/trans = 8/92) showed no evidence of interconversion of diastereomers. Thus, the build up during irradiation of a greater amount of thermodynamically favored *cis*-**7** irradiation than was initially present was not observed nor was a systematic drift in the ratio of products with conversion of **7** seen. In fact, the cis/trans ratios of phosphite diastereomers (8/92 and 43/57) was nearly unchanged at 24 and 72 h. (Interestingly, the diastereomers of **7** are consumed at nearly equal rates.) *Second*, the accountabilities of converted phosphite **7**, in terms of phosphonate **8** formed, are not quantitative. Therefore, for the conclusion regarding stereochemistry to be valid, the same fraction of side products must be formed from each diastereomer of **7**. The consistency of results and at several conversions, for two initial diastereomeric ratios of **7**, supports this conclusion.

Scheme 2 depicts for *cis*-**7** a mechanism that accounts for the observed stereochemistry at phosphorus (**16** → **17** → *cis*-**8**). Featured is the mode 4 (M_4) that was postulated previously for the triplet-sensitized photorearrangement of **5** to trap the otherwise reversibly formed **16**.[1c,d] Equation 2 shows the apical introduction of the 1,2-biradical-like[4] styryl moiety to form 1,3-biradical **16**.



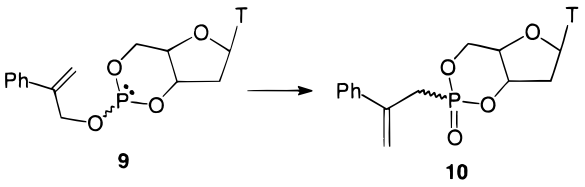
(2)

This stereochemistry is analogous to that for the *reversible* apical addition of alkyl radicals to trialkyl phosphites.[9] The trigonal bipyramidal geometry of **16** is based on the known structures of similar phosphoranyl *mono*-radicals.[10] It is significant that a mode 1 rearrangement of **16** to give **18** would lead to inversion of configuration at phosphorus and generation of *trans*-**8** (Scheme 2). The driving force for **16** → **17** (and **16** → **18**) is the known thermodynamic preference with phosphoranyl monoradicals for the oxygen and carbon substituents to be apical and equatorial, respectively. Presuming that rearrangement of **16** precedes β-scission to form *cis*-**8**, the stereochemical results of this study provide further evidence for the contrasting permutational properties of phosphoranyl radicals and truly pentacovalent phosphorus molecules. The latter exchange ligands via mode 1 processes. However, the possibility that **16** gives *cis*-**8** directly cannot be excluded since we have previously postulated that **16** → **17** is relatively slow.[1c,d]

Triplet-Sensitized Photorearrangement of Thymidine-Based Cyclic Phosphite 9. The triplet triphenylene-sensitized photolysis of 0.005 M solutions of phosphite **9** (35/65 cis/trans ratio) with light from the 350 nm lamps of a Rayonet reactor led to 37−41% consumption of the phosphite in 144 h but generated only 7−12% of phosphonate **10** (quantitative ^{31}P NMR; tri-*n*-propyl phosphate internal standard). The individual diastereomers of phosphonate **10**, however, can be prepared from

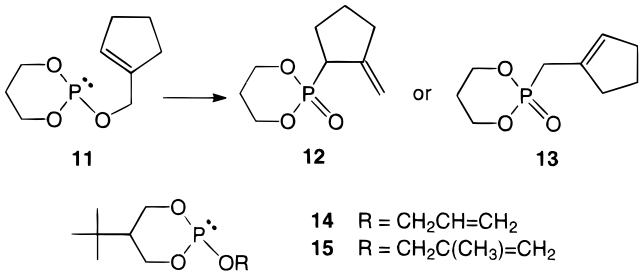
(7) Bentrude, W. G.; Hargis, J. H. *J. Am. Chem. Soc.* **1970**, *92*, 7136.
(8) See coverage in: Bentrude, W. G. In *Steric and Stereoelectronic Effects in 1,3,2-Dioxaphosphorinanes*; Juaristi, E., Ed.; VCH: New York, 1995; Ch. 7. Bentrude, W. G. In *^{31}P NMR Spectroscopy*; Verkade, J. G., Quin, L., Eds.; VCH Publishers: New York, 1987; Chapter 11. Maryanoff, B. A.; Hutchins, R. O.; Maryanoff, C. A. *Top. Stereochem.* **1979**, *11*, 187.
(9) Davies, A. G.; Dennis, R. W.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1101. Cooper, J. W.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2*, **1976**, 808.
(10) For the most recent reviews of the chemistry of phosphoranyl radicals, see: Bentrude, W. G. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; John Wiley and Sons: Chichester, 1990; Vol. 1, Chapter 14. Bentrude, W. G. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1983; Vol. 3, Chapter 4. Bentrude, W. G. *Acc. Chem. Res.* **1982**, *15*, 117. Roberts, B. P. In *Advances in Free Radical Chemistry*; Williams, G. H., Ed.; Heyden: London, 1979; Vol. 6, p 225.

9 by photoinduced single electron transfer (SET) methods.[11] (See Supporting Information.)

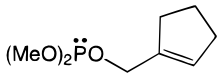


Reasonable yields of phosphonate **8** were obtained on irradiation of **7** over extended periods of time (4−5 days). The disappointing outcome with cyclic phosphite **9** obviously results from the highly inefficient nature of its photorearrangement. To a much greater degree than with phosphite **7**, which has phosphorus in a six-membered ring, phosphite **9** is converted to unidentified side products that are seen in the ^{31}P NMR spectra obtained following photolysis. The thymin-1-yl ring of **9** can be readily activated by triplet sensitizers. However, triplet triphenylene (E_T = 67 kcal/mol[12]) is not energetic enough to transfer energy to **9**, based on the reported E_T value (>73 kcal/mol) for thymidine 5′-monophosphate.[13] The reluctance of the $\pi-\pi^*$ triplet of **9** to rearrange to **10** allows other undefined photoprocesses to take over.

Attempted Triplet-Sensitized Photorearrangements of Other Cyclic Phosphites. A deoxygenated solution in cyclohexane of phosphite **11** (0.011 M), tri-*n*-propyl phosphate (internal standard) and 5% (v/v) *m*-xylene (sensitizer), irradiated through quartz at 254 nm, showed 89% consumption of **11** after 144 h. Numerous peaks were noted by GC; however, GC/MS failed to detect the molecular ions of phosphonates **12** or **13** (202 amu). ^{31}P NMR spectroscopy showed no evidence for their formation. Under the same conditions, phosphites **14** and **15** were consumed and formed many products. However, no GC/MS or ^{31}P NMR evidence for phosphonate formation was seen.



The failure of phosphites **14** and **15** to give the corresponding phosphonates is in contrast to the rearrangements of acyclic $(MeO)_2POCH_2CH{=}CH_2$ and $(MeO)_2POCH_2C(Me){=}CH_2$ that generate good yields of $(MeO)_2P(O)CH_2CH{=}CH_2$ and $(MeO)_2P(O)CH_2C(Me){=}CH_2$.[3] This is consistent with the greatly reduced quantum yields (ϕ_P) encountered for the photorearrangement of phosphite **5** (phosphorus in a six-membered ring) compared to that for **1**.[1c,d] However, since the relative quantum yield for photorearrangement of **19** was 15 times[3b] that of the acyclic phosphite $(MeO)_2POCH_2CH{=}CHMe$, it was anticipated that the same alkene moiety in **11** might lead to phosphonate formation. Evidently the expected increased lifetime and energy for the $\pi-\pi^*$ triplet of **11**[4] is not sufficient to overcome the energetically unfavorable, highly reversible nature of the cyclization of triplet **11** to form a 1,3-biradical intermediate analogous to **16** and its slow subsequent mode 1 isomerization.



19

Energy Diagram. The results of the above studies, along with those from a previous full paper[1d] and communication,[3b] prompted us to attempt to unify our understanding of the effects of structural change on the efficiency of these photorearrangements in terms of the energy diagram of Scheme 3 which is based on a 1,2-diradical model[4] for the $\pi-\pi^*$ triplet. (Relative energies in Scheme 3 are approximate.) Such a test of this model is especially important since no direct spectroscopic evidence for the intermediates of Schemes 1 and 2 exists. Effects to be explained include: (1) the negative effect of placement of phosphorus in relatively small (five-, six-, or seven-membered) ring; (2) the negative effect of methyl-substitution at the 1-allyl position; (3) the positive effect of phenyl or alkyl substitution at the 2-allyl position; and (4) the positive effect of placement of the allyl double bond in a five-membered ring. Very significantly, Scheme 3 also incorporates the mode 4 permutation set forth in Scheme 2 that is consistent with the observed stereochemistry at phosphorus in the present study.

The "1,2-biradical model" was first proposed by Caldwell et al.[4] to explain reactions emanating from $\pi\pi^*$ alkene triplets. In this view the carbon that bonds to phosphorus in Scheme 3 to form the triplet 1,3-biradical (e.g., **4** or **16**) functions essentially as a free alkyl monoradical. As will be seen, the structure−quantum efficiency results indeed fit quite well to this model. Shown, for purposes of illustration, are the *spiro* 1,3-biradicals I and II, formed from a cyclic phosphite such as **7** or **11**, with phenyl substitution at the 2-allyl position. For the sake of simplicity, product formation in Scheme 3 is assumed to occur after intersystem crossing to the S_o 1,3-biradical. At the ground state 1,3-biradical stage, the overall efficiency of the photorearrangement is determined by the rate constant for reversion to S_o phosphite in competition with successive mode four (M_4) permutation (I ⇄ II) followed by β scission of II to give allylphosphonate. If the permutation (reversible) and β scission (irreversible) are both rapid, then allylphosphonate formation competes readily with reformation of ground state (S_o) allyl phosphite resulting in a relatively high overall quantum yield, ϕ_P.

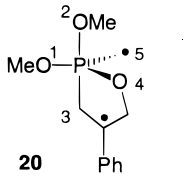
For dimethyl phosphites (e.g., **1** and the dimethyl analogues of **11**, **14**, and **15**) methyl substitution at the alkene terminus that bonds to phosphorus weakens the bond to phosphorus in the triplet and in the singlet 1,3-biradical increasing its ease of reversal to triplet (T_1) or ground state (S_o) phosphite (decreased ϕ_P[3b]). Phenyl (I and II),[1c,d] methyl, or ring carbon substituents[3b] at the 2-allyl position stabilize the 1,3-biradical and, furthermore, increase the rate of β scission of the S_o biradical to product allyl phosphonate by stabilizing the double bond

(11) See Supporting Information for preparation of **10** and separation of its diastereomers. (Sopchik, A. E.; Hager, D. H. *J. Org. Chem.* **2000**, *65*, 2778−2785.)
(12) Zander, M. *Z. Naturforsch., Teil A* **1984**, *39A*, 1145.
(13) Gut, I. G.; Wood, P. D.; Redmond, R. W. *J. Am. Chem. Soc.* **1996**, *118*, 2366.

being formed (increased ϕ_P). Cyclization to the triplet 1,3-biradical also is favored when the alkene moiety is in a small ring (**19**). The increased lifetime[4] of the planar $\pi-\pi^*$ T_1 optimizes the probability of cyclization to the triplet 1,3-biradical, rather than reversion to the ground state (S_o phosphite), and reversion to the $\pi-\pi^*$ T_1 is less energetically favorable (increased ϕ_P[3b]).

The permutation I ⇄ II pictured by the structures in Scheme 3 is for a spiro 1,3-biradical such as that from **5** or **7** which is postulated to be slow,[1c,d] as demonstrated experimentally for *spiro* phosphoranyl *mono*radicals;[6a,b] *its barrier is represented by the dotted line.* A low quantum yield for **5** → phosphonate formation results (ϕ_P = 0.002−0.003).[1c,d] Nonetheless, if phosphite **7** does undergo photo-Arbuzov rearrangement via initial formation of triplet biradical *cis*-**7**(T_1), eq 2, followed by permutational isomerization, the process analogous to I → II (**16** → **17**) is consistent with, though not required by, the observed stereochemistry *(cis*-**7** → *cis*-**8** and *trans*-**7** → *trans*-**8.**)

For monocylic (i.e., nonspiro) phosphoranyl radicals, ESR shows the M_4 process to be much more rapid[6] (*solid line* of Scheme 3). This allows, for example, the efficiency of trapping by permutational isomerization of **20** (formed from **1**), in competition with reformation of **1**, to be greatly improved via an efficient cascade analogous to I (CH_2 ap) → II (CH_2 eq) → allylphosphonate (For phosphite **2**, ϕ_P = 0.2−0.3)[1c,d]



20

Experimental Section

Preparation of Compounds. Anhydrous solvents were obtained by distillation under nitrogen: diethyl ether from sodium/benzophenone; methylene chloride from calcium hydride under argon; acetonitrile from calcium hydride. Photoreactions in C_6D_6 and $CDCl_3$ were deoxygenated by purging with argon. Cyclohexane was spectral grade. Reagents were from Aldrich Chemical Co. unless otherwise specified. Tri-*n*-propyl phosphate was distilled prior to use. Triphenylene was recrystallized from ethanol. Triethylamine and thymidine were used as received. 2-Phenylallyl alcohol,[14] 5-*tert*-butyl-2-chloro-1,3,2-dioxaphosphorinane,[7] and thymidine 3′,5′-cyclic *N*,*N*-dimethylaminophosphoramidite[15] were prepared by literature procedures. Unless otherwise stated, distillations were performed with a short-path apparatus. Radial chromatography employed 60 PF_{254} silica gel containing gypsum (EM Science). Column chromatography was performed on 60−200 mesh silica gel (EM Science).

Physical Methods. Melting points are uncorrected. *J* values given in the ^{1}H NMR spectral data refer to proton−proton coupling unless otherwise stated. A 60 s repetition rate was employed when monitoring the photoreactions by ^{31}P NMR to ensure the accuracy of the integrations. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA. GC-EIMS (70 eV) analyses utilized a 30 m × 0.25 fused silica capillary column. Reported intensities are percentages of the base peak intensity. Other low resolution EIMS (70 eV) as well as HRMS (EI, 70 eV) measurements utilized a standard inlet system. FABMS LSIMS measurements utilized a cesium ion gun. The GLC yields were determined with a flame ionization detector on a 20 m × 0.25 mm fused silica capillary column (RSL-150) with tri-*n*-propyl phosphate as internal standard.

Photoinduced Triplet Energy Transfer Initiated Rearrangement of 5-*tert*-Butyl-2-(2-phenylallyloxy)-1,3,2-dioxaphosphorinane (7). For example, under argon by glovebag techniques in a 100.0 mL volumetric flask, tri-*n*-propyl phosphate (110.4 mg, 0.493 mmol), 8/92 cis/trans phosphite **7** (151.4 mg, 0.857 mmol), and triphenylene (114.0 mg, 0.500 mmol) were diluted to volume with acetonitrile. (The cis/trans ratio of diastereomers of **7** had been determined by ^{31}P NMR.) Three quartz tubes (13 mm × 80 mm) were flushed with argon, capped with rubber septa, and transferred to the glovebag. Via syringe, 5.0 mL of the reaction solution were added to each tube. The tubes were then irradiated for 96 h with light from the 350 nm lamps of a Rayonet photochemical reactor. Reactions were directly monitored by syringe sampling at 0, 24, 48, 72, and 96 h. At each conversion, the moles of each diastereomer of unreacted **7** were determined by ^{31}P NMR, by reference to the internal standard, on aliquots of reaction solution transferred to an NMR tube in a glovebag under argon. Moles of the individual diastereomers of **8** formed were determined in the same way. Very rarely it was necessary to concentrate the samples under a slow stream of argon prior to quantitation by ^{31}P NMR. The yields of the individual diastereomers of **8** (tri-*n*-propyl phosphate internal standard) also could be determined by GLC on a sample carefully concentrated under argon, using a 20 m × 0.32 mm RSL-150 capillary column. In that event the individual diastereomers of remaining phosphite **7** were quantitated by GC in by slow syringe addition under argon to the reaction concentrate of approximately 1.1 equiv of a of *tert*-BuOOH in an organic solvent to convert **7** to the phosphate. Close agreement was found in results determined by the two methods. The data of Table 1 are based on the ^{31}P NMR method. The combined yield of both isomers of **8** at >99% conversion of **7** (96 h) was 55% (GC). The reaction mixture was purified by radial chromatography (100% ethyl acetate) to give 81 mg (0.28 mmol, 54% isolated yield) of 5-*tert*-butyl-2-oxo-2-(2-phenylallyl)-1,3,2-dioxaphosphorinane (**8**) as a mixture of diastereomers. The structures of isolated **8** were confirmed by comparison of their spectral parameters to those of independently synthesized **8** (see Supporting Information).

Photoinduced Triplet Energy Transfer Initiated Rearrangement of 2-(Cyclopenten-1-ylmethoxy)-1,3,2-dioxaphosphorinane (11). By a similar glovebag procedure under argon, a 50.00 mL cyclohexane solution of *m*-xylene (2.5 mL), tri-*n*-propyl phosphate (118 mg, 0.530 mmol), and 2-(cyclopentenyl-1-methoxy)-1,3,2-dioxaphosphorinane (119 mg, 0.592 mmol) was dispersed in three quartz tubes (13 mm × 80 mm). The tubes were irradiated for 144 h with 254 nm light from a Rayonet photochemical reactor. The reactions were sampled by GC at 0, 12, 24, 48, 96, and 144 h. Consumption of phosphite: 48 h (13%); 96 h (70%); 144 h (89%) (20 m × 0.32 mm RSL-150 capillary column). An array of product peaks was detected by GC, none of which contained a 202 amu characteristic M^+ of the phosphonates (GC/MS) **12** or **13**.

Photoinduced Triplet Energy Transfer Initiated Rearrangements of 5-*tert*-Butyl-2-allyloxy-1,3,2-dioxaphosphorinane (14) and 5-*tert*-Butyl-2-(2-methylallyloxy)-1,3,2-dioxaphosphorinane (15) were carried out in same way as that for **11**. (See Supporting Information.)

Triplet Energy Transfer Initiated Rearrangement of Thymidine Cyclic 2-Phenylallyl-3′,5′-phosphite (9). A 50.0 mL methylene chloride solution of triphenylene (55.1 mg, 0.241 mmol), tri-*n*-propyl phosphate (119.7 mg, 0.534 mmol), and thymidine cyclic 2-phenylallyl-3′,5′-phosphite, **9** (101.9 mg, 0.252 mmol), was dispersed under argon in 1.5 mL portions into four Pyrex NMR tubes (5 mm) fitted with 10/30 ground glass joints. The tubes were degassed on a vacuum line by four freeze−pump−thaw cycles (0.02 mmHg), flame sealed, and then irradiated for 144 h with light from the 350 nm lamps of a Rayonet photochemical reactor. The percent conversion, yields, and diastereomer ratios were determined by ^{31}P NMR by comparing the integrations of the starting material and the product cyclic phosphonates, in reference to the internal standard (tri-*n*-propyl phosphate). The yield of phosphonate **10** was in the range of 7−12% based on converted starting phosphite **9** with conversions ranging from 37 to 41%.

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5-*tert*-Butyl-2-oxo-2-(2-phenylallyl)-1,3,2-dioxaphosphorinane (8) was routinely prepared from the Arbuzov reaction of 5-*tert*-butyl-2-methoxy-1,3,2-dioxaphosphorinane.[15] (See Supporting Information for details).

Preparation of 5-*tert*-Butyl-2-(2-phenylallyloxy)-1,3,2-dioxaphosphorinane (7). A solution of 5-*tert*-butyl-2-chloro-1,3,2-dioxaphosphorinane[15] (33.2 g, 0.168 mol) in 500 mL of anhydrous ether, maintained at 0 °C, was stirred in a which had been rinsed with triethylamine and dried at 110 °C. To it was added, dropwise, a solution of triethylamine (18.7 g 0.185 mol) and 2-phenylallyl alcohol (23.4 g, 0.175 mol) in 150 mL of dry ether over a 2 h period. The amine salts were filtered away under argon, and the solvent was removed under reduced pressure. The colorless residue oil was purified by chromatography (radial chromatography, 50% ethyl acetate/hexane) which resulted in 30.1 g (0.102 mol, 61% yield) of a mixture of two isomers of phosphite **7**; by ^{31}P NMR, 4/96 (cis/trans). *cis*-**7**: ^{31}P NMR (121.4 MHz $CDCl_3$) δ 124.8; ^{1}H NMR (299.9 MHZ $CDCl_3$): δ 0.89 (s, 9 H), 2.05 (tt, ^3J = 3.9 Hz, ^3J = 12.0 Hz, 1 H), 3.85 (m, 2 H), 4.15−4.23 (m, 2 H), 4.75 (d, $^3J_{PH}$ = 8.7 Hz, 2 H), 5.46 (bs, 1 H), 5.56 (bs, 1 H), 7.30−7.42 (m, 3 H), 7.49−7.54 (m, 2 H); ^{13}C NMR (75.4 MHz $CDCl_3$): δ 27.36, 31.31 (d, $^4J_{CP}$ = 1.6 Hz), 45.99 (d, $^3J_{CP}$ = 4.6 Hz), 61.62, 64.67 (d, $^2J_{CP}$ = 19.6 Hz), 113.79, 126.25, 127.99, 128.45, 138.45, 144.95 (d, $^3J_{CP}$ = 5.1): *trans*-**7**: ^{31}P NMR (121.4 MHz $CHCl_3$) δ 132.4; ^{1}H NMR (299.9 MHz $CDCl_3$): δ 1.01 (s, 9 H), 1.72−1.79 (m, 1 H), 3.87−4.02 (m, 2 H), 4.27−4.35 (m, 2 H), 4.79 (d, $^3J_{PH}$ = 9.0 Hz, 2 H), 5.47 (bs, 1 H), 5.57 (bs, 1 H), 7.30−7.42 (3H), 7.49−7.54 (m, 2H); ^{13}C NMR (75.4 MHz $CDCl_3$): δ 28.32, 32.35, 45.05 (d, $^3J_{CP}$ = 8.25 Hz), 61.15 (d, $^2J_{CP}$ = 2.0 Hz), 64.75 (d, $^2J_{CP}$ = 20.1 Hz), 113.85, 126.21, 128.00, 128.50, 138.44, 144.98 (d, $^3J_{CP}$ = 4.9 Hz). GC EIMS (70 eV) *m*/*z* (relative intensity) 294 [M^+] (100), 279 [$M - CH_3]^+$ (1), 237 [M − *tert*-Bu] (28); $C_{16}H_{23}O_3P$; HRMS $[M]^+$ (calcd) 294.13848, (obsd) 294.13970. Anal. Calcd for $C_{16}H_{23}O_3P$: C, 65.33; H, 7.88. Found: C, 65.06; H, 7.89. (Mixture of isomers: cis/trans = 4/96)

Preparation of Thymidine Cyclic 2-Phenylallyl 3′,5′-Phosphite (9). A solution of thymidine 3′,5′-cyclic *N*,*N*-dimethylaminophosphoramidite[16] (0.30 g, 0.94 mmol), 1-*H* tetrazole (70 mg), and freshly distilled methylene chloride (30 mL) was stirred under argon while 2-phenylallyl alcohol (134 mg, 1.0 mmol) was added via syringe at a rate of one drop every 5 s. The reaction was stirred for a further 12 h. The solvent was removed under reduced pressure (0.05 mmHg). The residue was dissolved in 50% ethyl acetate−diethyl ether and passed through a column of 60−200 silica gel under argon. The first 250 mL of eluent was collected, and the solvent was removed under reduced pressure affording 253 mg (0.62 mmol, 66% yield) of a white solid; phosphite **9**, cis/trans = 36/64 (cis/trans), ^{31}P NMR. *cis*-**9**: ^{31}P NMR (202.4 MHz $CDCl_3$) δ 122.97; ^{1}H NMR (499.8 MHz $CDCl_3$):[16] δ 1.91 (d, J = 1.3 Hz, 3 H), 2.09 (ddd, J = 2.3 Hz, J = 8.1 Hz, J = 13.4 Hz, 1 H), 2.33 (ddd, J = 8.6 Hz, J = 11.0 Hz, J = 13.4 Hz, 1 H), 3.55 (ddd, J = 9.3 Hz, J = 10.2 Hz, J = 4.6 Hz, 1 H, H4′), 4.14 (dddd, J = 11.0 Hz, J = 8.1 Hz, J = 9.3 Hz, $^3J_{HP}$ = 1.4 Hz, 1 H), 4.21 (ddd, J = 4.6 Hz, J = 9.2 Hz, $^3J_{HP}$ = 9.6 Hz, 1 H), 4.25 (ddd, J = 10.2 Hz, J = 9.2 Hz, $^3J_{HP}$ = 2.5 Hz, 1 H), 4.77 (d, $^3J_{HP}$ = 9.6 Hz, 2 H), 5.39 (d, ^2J = 1.0 Hz, 1 H), 5.52 (d, ^2J = 1.0 Hz), 6.07 (dd, J = 8.6 Hz, J = 2.3 Hz, 1 H), 6.79 (d, J = 1.3 Hz), 7.22−7.62 (m, 5 H) 10.0 (bs, 1 H); ^{13}C NMR (125.7 MHz $CDCl_3$): δ 12.82, 36.32, 65.68 (d, $^2J_{CP}$ = 20.2 Hz), 66.38 (d, $^2J_{CP}$ = 3.8 Hz), 68.66 (C(3′)), 75.03 (d, $^3J_{CP}$ = 7.0 Hz), 81.95, 111.70, 115.02, 126.26, 128.25, 128.57, 134.89, 138.10, 144.59 (d, $^2J_{CP}$ = 4.3 Hz), 150.49 (C(2)), 163.94 (C(4)). *trans*-**9**: ^{31}P NMR ($CHCl_3$) δ 129.74: ^{1}H NMR (499.8 MHz $CDCl_3$): δ 1.94 (d, J = 1.2 Hz, 3 H), 2.27 (m, 2 H), 4.02 (dddd, J = 9.9 Hz, J = 8.9 Hz, J = 9.2 Hz, $^3J_{HP}$ = 1.1 Hz, 1 H), 4.03 (ddd, J = 9.5 Hz, J = 9.6 Hz, $^3J_{HP}$ = 8.7 Hz, 1 H), 4.14 (dddd, J = 9.2 Hz, J = 6.4 Hz, J = 9.5 Hz, $^4J_{HP}$ = 0.9 Hz, 1 H), 4.35 (ddd, J = 6.4 Hz, J = 9.6 Hz, $^3J_{HP}$ = 1.9 Hz, 1 H), 4.79 (d, $^3J_{HP}$ = 10.1 Hz, 2 H), 5.38 (d, ^2J = 1.2 Hz, 1 H), 5.54 (d, ^2J = 1.2 Hz, 1 H), 6.09 (dd, J = 4.6 Hz, J = 6.6 Hz, 1 H), 7.01 (d, J = 1.2, 1 H), 7.22−7.62 (m, 6 H) 10.0 (bs, 1 H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 12.75, 36.32, 65.04 (d, $^2J_{CP}$ = 19.8), 68.13 (d, $^2J_{CP}$ = 4.6), 70.07 (d, $^2J_{CP}$ = 4.5), 73.12 (d, $^3J_{CP}$ = 20.2), 82.84, 111.95, 114.66, 126.16, 128.25, 128.63, 135.24, 138.70, 144.54 (d, $^2J_{CP}$ = 4.3 Hz), 163.94. Anal. Calcd for $C_{19}H_{21}N_2O_6P$: C, 56.47; H, 5.23. Found: C, 56.41; H, 5.23. (Mixture of diastereomers: cis/trans = 36/64).

Preparation of 1-Hydroxymethylcyclopentene. A suspension of aluminum chloride (6.5 g, 0.048 mol) and lithium aluminum hydride (6.0 g 0.15 mol) in 500 mL of dry diethyl ether was stirred at 0 °C for 1 h. To it was added, dropwise, a solution of ethyl 1-cyclopentenecarboxylate[16] (20 g, 0.15 mol) in 50 mL of diethyl ether. After 2 h the reaction was quenched by the dropwise addition of 12 mL of water. After 1 h the suspension was filtered, and the organic phase was washed with saturated NaCl (3 × 100 mL). The filtrate was dried over $MgSO_4$ and filtered. The solvent was evaporated. The residue was distilled to give a colorless liquid (9.8 g, 0.097 mol, 70% yield, bp 60−62 °C at 4.0 mmHg [lit.[17] bp 60−62 °C at 10 mmHg]): ^{1}H NMR (299.9 MHz $CDCl_3$) δ 1.86−1.97 (m, 2H), 1.99 (bs, 1H), 2.27−2.40 (m, 4H), 4.19−4.21 (m, 2H), 5.60−5.63 (m, 1H).

Preparation of 2-(Cyclopenten-1-ylmethoxy)-1,3,2-dioxaphosphorinane (11). Under an argon atmosphere, a solution of 2-chloro-1,3,2-dioxaphosphorinane (500 mg, 2.55 mmol) in 50 mL of freshly distilled diethyl ether in a flask which had been rinsed with triethylamine and dried at 110 °C, was stirred at 0 °C. A solution of triethylamine (309 mg, 3.06 mmol) and 1-hydroxymethylpentene (275 mg, 2.80 mmol) in 25 mL of dry diethyl ether was added dropwise over 1 h. The amine salts were filtered away under argon, and the solvent was removed under reduced pressure. The clear liquid residue was purified by chromatography (Chromatotron, 30% ethyl acetate−hexane) to give 421 mg (1.63 mmol, 64% yield) of **11**, a colorless oil: ^{31}P NMR (121.4 MHz C_6D_6) δ 133.5; ^{1}H NMR (299.9 MHz C_6D_6) δ 0.71−0.81 (m, 1 H), 1.71−1.79 (m, 2 H), 1.95−2.15 (m, 1 H), 2.19−2.30 (m, 4 H), 3.38−3.49 (m, 2 H), 4.21−4.32 (m, 4 H), 5.61−5.65 (m, 1 H); ^{13}C NMR (75.4 MHz C_6D_6): δ23.40, 28.69 (d, $^3J_{CP}$ = 5.2 Hz), 32.46 ($CH_2CH_2CH_2$), 32.82, 59.35, 62.07 (d, $^2J_{CP}$ = 19.6 Hz), 127.26, 141.73 (d, $^3J_{CP}$ = 5.6 Hz). GC EIMS (EI-70 eV) *m*/*z* (relative intensity) 202 $[M]^+$ (2), 201 $[M - 1]^+$ (2), 81 $[M - C_3H_6PO_3]$(36), 80 $[M - C_3H_7PO_3]$ (100); EI HRMS $C_9H_{15}O_3P$ $[M]^+$: Anal. Calcd for $C_9H_{15}O_3P$: C, 53.45; H, 7.48. Found: C, 53.45; H, 7.55 (mixture of isomers).

5-*tert*-Butyl-2-allyloxy-1,3,2-dioxaphosphorinane (14) and 5-*tert*-butyl-2-(2-methylallyloxy)-1,3,2-dioxaphosphorinane (15) were prepared by the method used for **7** and **11**. (See Supporting Information.)

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Supporting Information Available: Procedures for the preparation and separation of the diastereomers of phosphonates **8** and **10**, the attempted triplet-sensitized rearrangements of **14** and **15**, and the preparations of **14** and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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