

# Photo-Arbusov Rearrangements of Dimethyl Benzyl and Dimethyl *p*-Acetylbenzyl Phosphite

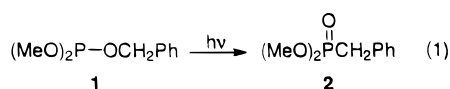
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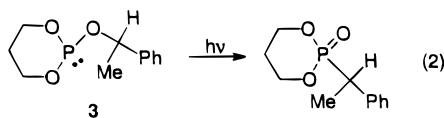
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**Abstract:** The direct ultraviolet irradiation of dimethyl benzyl phosphite (**1**) and dimethyl *p*-acetylbenzyl phosphite (**8**) was investigated in acetonitrile, cyclohexane, and benzene. Phosphite **1** gives predominantly the photo-Arbusov product, dimethyl benzylphosphonate (**2**), in 67–81% accountability yields, based of phosphite consumed, along with *minor amounts* of bibenzyl (**20**) and dimethyl phosphite (**10**). The quantum yield for formation of **2** in cyclohexane,  $\phi_p$ , is 0.43. By contrast, irradiation of phosphite **8** yields only 7–13% of photo-Arbusov phosphonate (**9**) but relatively *large amounts* of radical diffusion products: dimethyl phosphite (**10**) the *p*-acetylbenzyl radical dimer (**11**); and *p*-acetyltoluene (**12**). Evidently **8**, closely related to acetophenone, reacts predominantly via the triplet excited state to generate long-lived, *triplet*, free-radical pairs (**6** and **7a**). In benzene, further products (**15**, **16**, **17a** and **17b**) are identified that result from addition of the phosphinoyl radical (**6**) to benzene to give cyclohexadienyl radical **14**, followed by combination and disproportionation reactions with radical **7a**. (Total product quantum yields in benzene ( $\Sigma\phi_i$ ) = 0.47.) In benzene, accountabilities of radical **6** from photolysis of **8** as high as 56% are encountered along with up to 92% accountabilities of *p*-acetylbenzyl (**7a**) radicals. Addition of radical scavengers PhSH, PhCH<sub>2</sub>Br, and TEMPO in the three solvents establishes the *cage yield* of **9** as 3–5%. The products of radical trapping provide further proof of the radical-pair nature of the photolysis of phosphite **8**, including a 95% accountability of **6** with PhCH<sub>2</sub>Br in benzene. It is proposed that the CH<sub>2</sub>–O scission of triplet **8** must occur concertedly with partial phosphoryl (P=O) bond formation. The trapping of radicals **6** and **7b** from irradiation of phosphite **1** as the benzene adducts **22** and **23**, analogous structurally to those (**16** and **17**) from phosphite **8**, supports the postulation that photoisomerization of **1** to **2** proceeds via short-lived, presumably *singlet*, free-radical pairs.

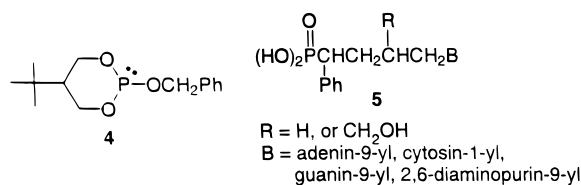
We have published preliminary reports<sup>1,2</sup> of the rearrangement, on direct irradiation with ultraviolet light, of dimethyl benzyl phosphite (**1**) to the isomeric benzylphosphonate **2**.



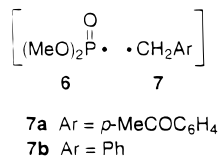
This rearrangement is *formally* a 1,2-sigmatropic shift. It can be termed a photo-Arbusov rearrangement. By use of phosphites **3** and **4**, we were able to establish the stereochemistry of the



process both at phosphorus (retention)<sup>2</sup> and at the migratory carbon (primarily retention).<sup>1</sup> This new reaction has been successfully applied to the preparation of acyclic nucleoside-based phosphonates, **5**.<sup>3,4</sup> Moreover, CIDNP<sup>5</sup> and CIDEP<sup>6</sup>



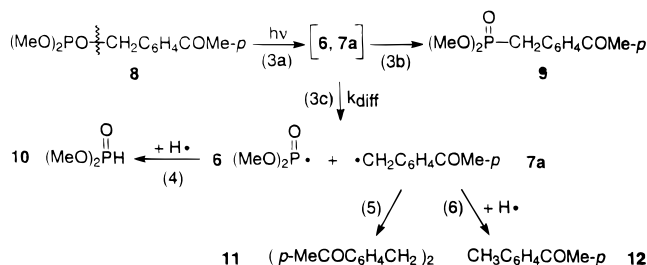
studies of the potential formation of radical pairs (**6** and **7**) in the photorearrangements of phosphites **1** and **8** and the 1-naphthylmethyl analogue of **1** have been published.



In this paper we report detailed product studies of the photorearrangements of **1** and **8** in cyclohexane, acetonitrile, and benzene, along with quantum yields for product formation

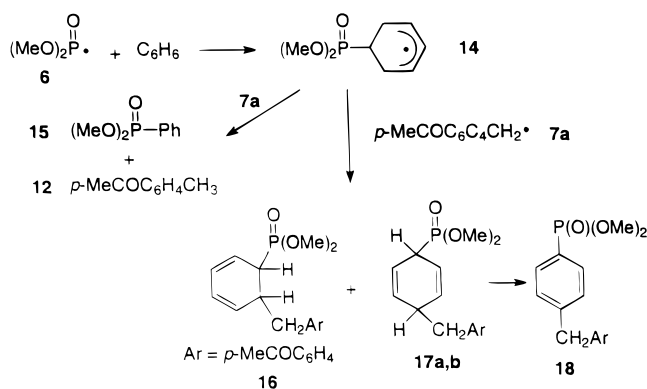
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Scheme 1<sup>a</sup>

<sup>a</sup> Equations are numbered in parentheses.

## Scheme 2



in benzene. The low yield of phosphonate **9** from **8** and the major effects on product distribution of added free-radical traps PhSH, PhCH<sub>2</sub>Br and TEMPO are defined. The photolysis of **8** evidently proceeds primarily, and perhaps totally, via the relatively long-lived triplet radical pair **6** and **7a** (Ar = *p*-acetylphenyl) that can be diverted by scavengers to phosphite **10**, phosphorobromide **13**, and *p*-acetyltoluene (**12**) and establish a cage yield of phosphonate **9** of 3–5%. In addition the chemistry of the phosphinoyl radical-benzene adduct, the cyclohexadienyl radical **14**, in the presence of the relatively stable *p*-acetylbenzyl radical is defined (Scheme 2).

The contrasting product distributions found for phosphites **1** and **8** argue for the primarily singlet nature of the photorearrangement of **1**. Thus, the photorearrangement of **1** gives phosphonate **2**, as the primary product, and also generates small amounts of free-radical-derived products, for example bibenzyl (**20**) and phosphite **10**. This process is most simply interpreted as proceeding through short-lived, singlet radical pair **6** and **7b** (Ar = Ph) that largely combine in the solvent cage to form phosphonate **2**. The formation of radical pairs in the photochemistry of **1** and **8** finds broader relevance in the context of the extensive recent studies of the formation of ion and radical pairs on photolysis of arylmethyl and diaryl methyl derivatives, including halides and esters.<sup>7</sup>

## Results

**Photoreaction of 8.** Irradiation (450 W medium-pressure UV lamp) through a uranium filter ( $\lambda > 320$  nm) of 0.016–0.030 M deoxygenated solutions of **8** in the solvents cyclohexane and acetonitrile yielded phosphonate **9** in minor amounts (7–8%), along with **10–12** (gas chromatography (GC) analysis). Ac-

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Table 1. Products of Photoreaction of **8** (0.016–0.030 M)

solvent	% conv. of <b>8</b>	product accountability, % <sup>a</sup>							
		<b>9</b>	<b>10</b>	<b>11</b> <sup>b</sup>	<b>12</b>	<b>15</b>	<b>16</b>	<b>17a</b>	<b>17b</b>
CH <sub>3</sub> CN	14	7.5	7.8	18	13				
CH <sub>3</sub> CN	25	7.2	5.4	17	9.4				
CH <sub>3</sub> CN	45	7.3	6.8	16	7.5				
CH <sub>3</sub> CN	65	7.5	3.5	15	7.0				
cyclohexane	18	7.1	9.4	13	9.8				
cyclohexane	25	6.9	8.6	12	9.4				
cyclohexane	41	7.0	6.6	12	8.3				
cyclohexane	55	7.0	8.8	13	7.4				
benzene	11	13	c	38	14	16	8.6	8.9	9.6
benzene	28	10	c	32	8.7	13	6.8	7.6	8.3
benzene	53	9.3	c	30	7.7	12	5.5	6.6	7.4
benzene	77	9.3	c	30	7.9	13	4.7	5.7	6.8

<sup>a</sup> Based on consumed **8**. <sup>b</sup> Yield of **11** doubled to account for the stoichiometry of its formation from **8**. <sup>c</sup> Not observed.

Table 2. Products of Ultraviolet Light Irradiation of **1** (0.010–0.012 M)

solvent	% conv. of <b>1</b>	product accountability, % <sup>a</sup>		
		<b>2</b>	<b>20</b> <sup>b</sup>	<b>15</b>
CH <sub>3</sub> CN	14	81	12	
	26	80	8.4	
	59	68	6.2	
	83	67	6.8	
	83	67	6.8	
cyclohexane	14	71	6.2	
	35	68	5.6	
	62	64	5.6	
	80	65	5.8	
	80	65	5.8	
C <sub>6</sub> H <sub>6</sub>	14	62	8.6	1.4
	30	54	6.0	1.5
	46	57	6.0	1.5
	60	55	5.8	1.5
	60	55	5.8	1.5

<sup>a</sup> At  $\geq 65\%$  conversion of **1** CH<sub>3</sub>CN and cyclohexane, 4–8% of **10** was observed. <sup>b</sup> Yield of the dimer (**20**) was doubled to account for the stoichiometry of its formation from **1**.

countability yields of those products at various conversions of phosphite **8** are recorded in Table 1. The yield of phosphonate **9** (the photo-Arbusov product) is dramatically reduced from the phosphonate yields found in previous work on the photorearrangements of arylmethyl phosphites including a preliminary study of phosphite **1** (see subsequent discussion, and Table 2) **1** and **2**. Clearly, radical pair **6** and **7a** (Ar = *p*-acetylphenyl) is formed on photolysis of **8** and undergoes predominant diffusional separation as shown (Scheme 1, eq 3). Modest yields of products generated from radicals **6** and **7a** are detectable by GC analysis: dimethyl phosphite **10** (eq 4), dimer **11** (eq 5), and *p*-acetyltoluene **12** (eq 6). Based on consumed **8**, the overall accountability of phosphinoyl radical **6** as products **9** and **10** is 11–17%. Products **9**, **11** and **12** account for 27–39% of the *p*-acetyl radicals potentially generated.

In addition, numerous very small identified peaks are seen on GC analysis of the photolyzates generated in cyclohexane and acetonitrile. They amount, however, to only 15–20% of the total product peak area, including identified products. <sup>31</sup>P NMR spectra of photolyzates also display numerous unidentified resonances. Products with known chemical shifts<sup>8</sup> that could result from dimerization of phosphinoyl radical **6** were not evident: (MeO)<sub>2</sub>P(O)–(O)P(OMe)<sub>2</sub>,  $\delta$  +8; (MeO)<sub>2</sub>P(O)–OP(OMe)<sub>2</sub>,  $\delta$  130 and –10. Photolyzate from irradiation of **8** in acetonitrile shows a very broad peak under the resonance for phosphonate **9** suggestive of polymer formation or a myriad of phosphonates in small quantities. The possibility remains as well that some dimerization of radicals **6** and **7b** takes place by attack on the phenyl ring of **7b**.

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**Table 3.** Effects of Scavengers PhSH and TEMPO on the Photoreaction of **8** (0.014–0.018 M) at 15–20% Conversion of **8**

solvent	scavenger	scavenger/ <b>8</b>	product accountability % <sup>a</sup>				
			<b>9</b>	<b>10</b>	<b>11</b> <sup>b</sup>	<b>12</b>	<b>15</b>
CH <sub>3</sub> CN	PhSH	0	9.7	9	22	10	
CH <sub>3</sub> CN	PhSH	0.25	2.7	35	7	33	
CH <sub>3</sub> CN	PhSH	0.5	2.7	37	6	42	
CH <sub>3</sub> CN	PhSH	1.0	2.7	45	0	47	
cyclohexane	PhSH	0	8.3	6	18	7.5	
cyclohexane	PhSH	0.24	4.8	27	8	36	
cyclohexane	PhSH	0.29	4.3	31	0	42	
cyclohexane	PhSH	0.98	4.1	41	0	47	
C <sub>6</sub> H <sub>6</sub>	PhSH	0	9.0	0	31	10	13
C <sub>6</sub> H <sub>6</sub>	PhSH	0.47	3.9	11	4	51	23
C <sub>6</sub> H <sub>6</sub>	PhSH	1.1	3.4	12	0	53	20
cyclohexane	TEMPO	0	8.3	9.4	12	9.6	
cyclohexane	TEMPO	0.09	5.2	3.4	8	6.7	
cyclohexane	TEMPO	0.25	4.6	3.0	4	2.0	
cyclohexane	TEMPO	2.0	4.3	0	2	0	

<sup>a</sup> Based on consumed **8**. <sup>b</sup> Yield of **11** doubled to account for the stoichiometry of its formation from **8**.

Although phosphonate **9** is generated in 9–13% yields in benzene, certain of the photoproducts of **8** (Table 1) are very different from those formed in cyclohexane and acetonitrile. This results from the addition of phosphinoyl radical **6** to benzene to form the cyclohexadienyl adduct **14** (Scheme 2), a well-established process.<sup>9</sup> The *p*-acetylbenzyl radical (**7a**) almost certainly stems from the disproportionation reaction of *p*-acetylbenzyl radical (**7a**) with **14**.

Thus, when the solvent is C<sub>6</sub>D<sub>6</sub>, deuterated (CH<sub>2</sub>D) **12** is formed exclusively (GC/MS). Notably, dimethyl phenylphosphonate (**15**) is generated in the same step and accounts for 12–16% of the phosphinoyl radicals (**6**) potentially generated from **8**. Cross-combination of *p*-acetyl radical **7a** with radical **14** competes ably with disproportionation and gives two products in combined yields of 17–26%: **16**, as a single isomer, and **17** as diastereomers (**17a** and **17b**), whose specific *cis* or *trans* geometries have not been assigned. Together, photo-Arbuzov product **9**, phosphonate **15**, and radical combination products **16** and **17** account for 39–56% of the phosphinoyl radicals (**6**) potentially formed in benzene. Interestingly, no phosphite **10** was detected in benzene, perhaps because of the rapid formation of **14**.

Photolysis of **8** in C<sub>6</sub>D<sub>6</sub> results in incorporation of deuterium, in accordance with Scheme 2, into the molecular ions and fragment ions (GC/MS) of not only product **12**, but also **15**, **16**, **17a** and **17b**. In benzene *p*-acetylbenzyl radicals (**7a**) not trapped as **12**, **16**, and **17** combine to yield dimer **11** (Scheme 1, eq 5) in increased accountability yields (30–38%) over those generated (12–18%) in cyclohexane and acetonitrile. The accountability of *p*-acetylbenzyl radicals in benzene is 38–52%, when based solely on products **11** and **12**, but totals 65–92% when photo-Arbuzov phosphonate **9** and radical combination products **16** and **17** are included. (In accounting for *p*-acetylbenzyl radicals, the accountability of **11** recorded in Tables 1 and 3–5 is twice the actual yield to reflect the stoichiometry of its formation.)

Products **17a** and **17b**, formed randomly in roughly equal amounts (7–10% each at 11 and 28% conversions, Table 1), are prone to aromatization to **18** on standing at room temperature in solution and on isolation by HPLC. Nonetheless, <sup>31</sup>P NMR spectra and both low and high-resolution mass spectra of **16**, **17a**, and **17b** (GC/MS) were obtained on the photolyzate.

Cyclohexadiene **16**, a single diastereoisomer, was isolated by high-performance liquid chromatography (HPLC), but **17a** and **17b** were isolated only as aromatized product **18**. The structures of **16**, **17a**, **17b**, and **18** were assigned by LRMS, HRMS, <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopy (see Experimental).

Thus, in addition to the molecular ion, the mass spectrum of **16** shows major peaks corresponding to the loss of *p*-acetylbenzyl (base peak), the loss of (MeO)<sub>2</sub>P(O), and the formation of the (MeO)<sub>2</sub>P(O) cation. Evidence for the 1,3-cyclohexadiene ring is seen in the NMR spectra of **16**, which display four distinctly different olefinic proton resonances (δ 5.42–5.82) and four corresponding <sup>13</sup>C resonances (δ 119.5–128.9) that exhibit phosphorus–carbon couplings (5.8, 6.2, 12.4, and 12.8 Hz). The allylic proton at the ring carbon attached to phosphorus gives a broad multiplet at δ 2.62 which contains a predictably large (29.6 Hz) <sup>2</sup>J<sub>PH</sub> coupling.<sup>10</sup> Its allylic neighbor proton (δ 3.04), located at the point of attachment of the *p*-acetylbenzyl group, displays a multiplet that includes a 21.7-Hz coupling to phosphorus (<sup>3</sup>J<sub>PH</sub>) in addition to 7.2- and 8.3-Hz couplings to the adjacent diastereotopic benzyl protons. The allylic carbons display assignable 133.6 (<sup>1</sup>J<sub>PC</sub>) and 4.1 Hz (<sup>2</sup>J<sub>PC</sub>) phosphorus–carbon coupling constants.<sup>11</sup> Significantly, the benzylic carbon displays a three-bond 24.0-Hz coupling to phosphorus which, along with the presence of the four vinylic <sup>1</sup>H and <sup>13</sup>C resonances noted earlier, shows that ArCH<sub>2</sub> and (MeO)<sub>2</sub>P(O) are attached 1,2 rather than 1,3 on the cyclohexadiene ring. The methoxy groups of **16** are diastereotopic in both the proton and carbon spectra, reflecting the presence of the adjacent stereogenic allylic carbon. The benzylic hydrogens of **16** are also diastereotopic and generate an AMX spectrum with a geminal proton–proton coupling (<sup>2</sup>J<sub>HH</sub> = –13.4 Hz) along with the proton–proton couplings to the adjacent allylic ring proton (<sup>3</sup>J<sub>PH</sub> = 7.2, 8.3 Hz) seen in the <sup>1</sup>H NMR spectrum of that proton.

The individual isomers **17a** and **17b** show the same major GC/MS peaks as **16** except for the absence of a mass corresponding to loss of (MeO)<sub>2</sub>P(O). The <sup>31</sup>P chemical shifts for **17a** and **17b** at δ 25.97 and 26.30 are consistent with their allylphosphonate structures.<sup>12</sup> Unlike **16**, **17**, and **17b**, the aromatized phosphonate **18** does not display significant peaks in its mass spectrum from scission of bonds to the *p*-acetylbenzyl or (MeO)<sub>2</sub>P(O) groups, but instead gives a base peak at *m/z* = 303 from loss of methyl and no other assignable peaks of relative intensity greater than 2% of the base peak. The <sup>31</sup>P NMR resonance of **18** at δ 23.7 is representative of phenylphosphonates such as **15**.<sup>13</sup> The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **18** affirm its highly symmetrical nature and the presence of two *p*-substituted benzene rings (see Experimental Section).

The single diastereomer of **16** is predicted to be the *trans* isomer, formed in a transition state for coupling which avoids steric interactions between the two large groups. Consistent with this idea is the large value (24.0 Hz) noted earlier for the three-bond coupling between the benzylic carbon of **16** and phosphorus that appears to require a very large C–C–P dihedral angle.<sup>11</sup> The simultaneously large <sup>3</sup>J<sub>PH</sub> value (21.7 Hz) we assign to the proton at the point of ring attachment of the arylmethyl, however, argues for an antiperiplanar arrangement of phosphorus and hydrogen<sup>12</sup> attainable only with the *cis* isomer (Dreiding models).

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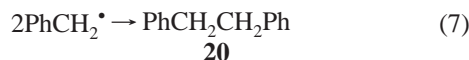
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**Table 4.** Effects of Added PhCH<sub>2</sub>Br as Scavenger on the Photoreaction of **8** (0.015 M) at 15–18% Conversion in CH<sub>3</sub>CN and Cyclohexane

solvent	PhCH <sub>2</sub> Br/ <b>8</b>	product accountability % <sup>a,b</sup>						
		<b>2</b>	<b>9</b>	<b>11</b>	<b>12</b>	<b>13</b>	<b>20</b>	<b>21</b>
CH <sub>3</sub> CN	0		7.6	17	10	0	0	0
CH <sub>3</sub> CN	0.5	3.8	16	42	0	67	19	24
CH <sub>3</sub> CN	2	3.5	8.7	30	0	68	19	22
CH <sub>3</sub> CN	8	3.9	7.1	36	0	69	26	28
CH <sub>3</sub> CN	15	3.6	4.0	32	0	76	28	23
CH <sub>3</sub> CN	23	1.7	3.5	32	0	79	32	23
cyclohexane	0		7.2	16	8.6	0		
cyclohexane	0.52	4.1	17	32	0.5	61	18	21
cyclohexane	4.1	2.6	11	30	0	69	24	23
cyclohexane	19	2.0	7.5	24	0	71	22	21
cyclohexane	46	1.9	5.0	22	0	84	24	23

<sup>a</sup> Based on consumed **8**. <sup>b</sup> Yield of **11** and **20** doubled to account for stoichiometry of formation from **8**.

**Photoreaction of 1.** Thoroughly deoxygenated 0.010–0.012 M solutions of phosphite **1** in cyclohexane, benzene, and acetonitrile were irradiated through quartz with 254 nm UV light. Identified products formed are recorded in Table 2 as a function of phosphite consumed (GC analysis). Accountabilities of reacted phosphite in terms of product phosphonate **2** (eq 1) demonstrate a small decrease with increased phosphite conversion. However, irradiation of **2** shows it to be photostable over time periods comparable to those required for rearrangement of **1** to **2**. Notable are the good accountability yields of **2** (e.g., 67–81% at 14–83% conversion in acetonitrile) along with modest accountabilities of benzyl radicals (6–12%) as bibenzyl (**20**), eq 7. This is in marked contrast to the radical diffusion



products that dominate the photochemistry of phosphite **8** (Table 1). Unfortunately, toluene (**19**), potentially formed in minor amounts (eq 8), eluted with solvent under the GC conditions



and could not be assayed. Phosphite **10** becomes detectable at conversions of 65% and above in 4–8% yields in acetonitrile and cyclohexane, but not in benzene. These accountabilities of **10** are somewhat less than those seen from photolysis of **8** even at low conversions of **8** (Table 1).

Although 20–30% of the phosphorus of phosphite **1** remains unaccounted for in acetonitrile and cyclohexane, the <sup>31</sup>P NMR spectra of photolyzate solutions run at high signal-to-noise showed the absence of any but very small peaks in addition to **6**. GC analysis showed minute peaks at long retention times. It was noted earlier that a large number of unidentified products are generated in small quantities in these solvents on photolysis of **8**. From **8** approximately 95% of the initial pairs diffuse from the solvent cage, and only a few percent recombine randomly to form **9**. In acetonitrile and cyclohexane, only bibenzyl (**20**) and dimethyl phosphite (**10**) are identifiable. The failure to account for the missing radicals **6** and **7b** from **1**, therefore, is not surprising. The possibility of formation of polymers or other high-boiling side products from both **1** and **8** remains.

**Scavenger Studies.** Recorded in Tables 3–5 are representative data showing the effects on the distribution and yields of products from photolysis of **8** of adding a range of concentra-

**Table 5.** Effects of Added PhCH<sub>2</sub>Br as Scavenger on the Photoreaction of **8** (0.015 M) at 15–18% Conversion in C<sub>6</sub>H<sub>6</sub>

solvent	PhCH <sub>2</sub> Br/ <b>8</b>	<b>9</b>	<b>11</b>	<b>12</b>	<b>13</b>	<b>15</b>	<b>16</b>	<b>17a</b>	<b>17b</b>	<b>20</b>	<b>21</b>	<b>22</b>	<b>23</b>
C <sub>6</sub> H <sub>6</sub>	0	12	38	12	0	12	8.9	8.9	9.3	0	0	0	0
C <sub>6</sub> H <sub>6</sub>	3.7	10	38	0	38	4.5	2.6	2.7	2.9	13	23	1.1	2.7 <sup>d</sup>
C <sub>6</sub> H <sub>6</sub>	7.4	7.0	36	0	43	0	1.7	1.9	1.9	17	26	1.1	2.5
C <sub>6</sub> H <sub>6</sub>	20	5.3	32	0	83	0	c	c	c	22	26	c	c
C <sub>6</sub> H <sub>6</sub>	30	4.5	34	0	84	0	c	c	c	20	24	c	c
C <sub>6</sub> H <sub>6</sub>	51	4.5	34	0	95	0	c	c	c	24	26	c	c

<sup>a</sup> Based on consumed **8**. <sup>b</sup> Yields of **11** and **20** doubled to reflect stoichiometry of formation from **8**. <sup>c</sup> <1% yield. <sup>d</sup> Isomers **23a** and **23b** are present in approximately equal amounts (<sup>31</sup>P NMR).

tions of free radical scavengers PhSH (0.0035–0.017 M), benzyl bromide (0.007–0.70 M), and TEMPO (0.0016–0.034 M).

**Thiophenol.** Even at low concentrations (PhSH/**8** = 0.3–1.1), thiophenol diverts *p*-acetylbenzyl radicals (**7a**) to *p*-acetyloluene (**12**) (highest **12** accountability yields: 47%, acetonitrile; 53%, benzene) to the exclusion of *p,p'*-diacetyl-bibenzyl (**11**) and radical combination products **16** and **17** (Scheme 1, eq 6, PhSH as H-donor). The same effect is seen in cyclohexane even at PhSH/**8** = 0.29 (yield of **12**, 42%). Phosphonate **9** accountabilities are leveled out in all three solvents at 3–4% at 0.5–1.0 ratios of PhSH/**8**. Phosphinoyl radical **6** is increasingly trapped (eq 4, PhSH as H-donor) as dimethyl phosphite (**10**) as the amount of added PhSH increases (maximum yields in acetonitrile and cyclohexane: 45 and 41%, respectively). The reasonably good yields of **10** and *p*-acetyloluene (**12**) in acetonitrile and cyclohexane found with PhSH added are especially significant, as the accountabilities of radicals **6** and **7a** (Ar = *p*-MeCOC<sub>6</sub>H<sub>4</sub>) are low in these solvents in the absence of a scavenger. The yield of **10** in benzene, however, at a 1.1 ratio of PhSH/**8** is seen to be only 12%. Moreover, phenylphosphonate **15** (Scheme 2) is formed in increased amounts on PhSH addition and persists in 20% yield at 1.1 PhSH/**8** (Table 3). Even at PhSH/**8** = 5.7 (0.09 M PhSH concentration; data not given in Table 3), a 10% yield of **15** was measured.

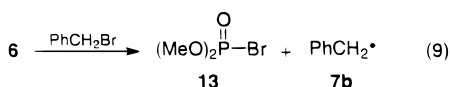
Under photolysis conditions, PhSH gives rise to PhSSPh and side products **29a**, **29b**, and **29c**, typical of the known<sup>14</sup> thermal Arbusov-like reaction of PhSSPh with phosphites. Products **29a** and **29b** also could result from combination of phenylthiyl radicals with radicals **6** and **7a**. (GC, GC/MS, and <sup>31</sup>P NMR evidence; see Supporting Information for structures **29a**–**29c**, their independent preparation, and characterization). The reaction of PhSSPh with **8** was confirmed in acetonitrile by a dark-reaction control and precluded the use of high concentrations of PhSH, even at low photochemical conversions of **8**. Thus, the 10% yield of phosphonate at 0.09 M PhSH, given in the previous paragraph, is somewhat low. Indeed, the less-than-quantitative accountabilities of radicals **6** and **7a** of Table 3 are in part a result of this side reaction of **8** with PhSSPh or scavenging by phenylthiyl radical.

A possible photochemical side-product of phosphonate **9** in the presence of PhSH is the alcohol *p*-MeCH(OH)C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>P(O)(OMe)<sub>2</sub>, potentially formed on reduction of the carbonyl functionality. Although GC/MS evidence for the generation of this product was obtained on extended irradiation of phosphonate **9** with PhSH, it was not formed (GC) under the reaction conditions used for the photorearrangements of **8** with PhSH added.

**Benzyl Bromide.** When added in sufficient amounts (PhCH<sub>2</sub>-Br/**8** ≥ 2 in CH<sub>3</sub>CN and cyclohexane; PhCH<sub>2</sub>Br/**8** ≥ 7.4, benzene) to the photoreactions of **8** in all three solvents, benzyl

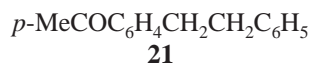
(14) Harvey, R. G.; Jacobson, H. J.; Jensen, E. V. *J. Am. Chem. Soc.* **1963**, *85*, 1618.

bromide diverts phosphinoyl radicals (**6**) that escape geminate recombination with **7a** (Ar = *p*-acetylphenyl) to phosphorobromidate **13** via a known reaction (eq 9)<sup>15</sup> in very good



accountabilities: 69–84% in cyclohexane and acetonitrile; 43–95% in benzene (Tables 4 and 5). (Photoirradiations were run with light from a 450 W medium-pressure UV lamp filtered through a uranium glass filter to remove light of wavelengths shorter than 320 nm and preclude any photolysis of benzyl bromide, even at high concentrations.) Even at low concentrations of PhCH<sub>2</sub>Br, dimethyl phosphite (**10**), normally seen in cyclohexane and acetonitrile, is absent. In benzene at concentrations greater than 0.1 M (PhCH<sub>2</sub>Br/**8** ≥ 7.4), PhCH<sub>2</sub>Br reduces the yield of PhP(O)(OMe)<sub>2</sub> (**15**) to zero. Indeed, even at modest PhCH<sub>2</sub>Br/**8** ratios, the accountability of phosphinoyl radical **6** as phosphorobromidate **13** is greatly improved over that found when PhSH is used to divert **6** to phosphite **10** (Scheme 1, eq 4). (See the yields of (MeO)<sub>2</sub>P(O)H (**10**) given in Table 3: 41 and 45% in cyclohexane and acetonitrile, respectively; PhSH/**8** = 1.0). Interestingly, low concentrations of added benzyl bromide in cyclohexane and acetonitrile increase the yield of phosphonate **9** from 7 to 8% to 16–17%.

Under benzyl bromide-scavenging conditions in cyclohexane and acetonitrile, the yield of *p*-acetyl toluene is reduced to zero at relatively low concentrations of the bromide (PhCH<sub>2</sub>Br/**8** ≥ 0.5). *p*-Acetylbenzyl radicals couple to form increased quantities of dimer **11** and also scavenge benzyl radicals, generated by reaction 9, to form the cross-coupling product **21**. The account-



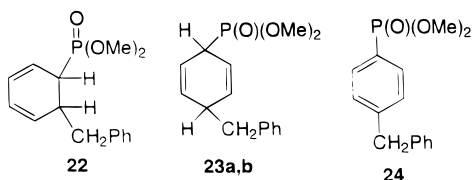
ability of *p*-acetylbenzyl radicals, taking into account the stoichiometry of product formation, is increased even at PhCH<sub>2</sub>Br/**8** = 0.5 and is in the range of 52–82% over the range of PhCH<sub>2</sub>Br concentrations used (Table 4).

The benzyl radicals (**7b**) formed in reaction 9 lead, in cyclohexane and acetonitrile, to 2–4% of the radical coupling product dimethyl benzylphosphonate (**2**, eq 10), bibenzyl (**20**,



eq 7), and cross-coupling product **21**. Bibenzyl (**20**) and cross-dimer **21**, but not **2**, are formed in benzene (Table 5). In benzene benzyl radicals also trap intermediate **14** to give the benzyl analogues (**22**, **23a**, and **23b**) of **16**, **17a**, and **17b** in 1–2% yields each. (Product **24** not formed under GC conditions.) Accountabilities of *p*-acetylbenzyl radicals are 46–62% in benzene. At relatively high concentrations of benzyl bromide (PhCH<sub>2</sub>Br/**8** ≥ 51, Table 5), the only remaining phosphorus-containing material in benzene is phosphonate **9** (4–5%), which is accompanied in cyclohexane and acetonitrile by 2–4% of benzylphosphonate **2**.

The structures of **22**, **23a**, and **23b** were confirmed by the



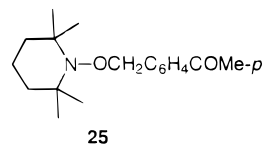
close similarity of their GC/MS fragmentation patterns to those

(15) Anpo, M.; Sutcliffe, R.; Ingold, K. U. *J. Am. Chem. Soc.* **1983**, *105*, 3580.

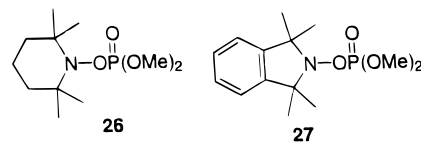
of **16**, **17a** and **17b** (see Experimental Section). Unlike the *cis/trans* isomeric **17a** and **17b**, only a single peak in the GC was observed for the benzyl counterparts **23a** and **23b** that do, however, display different <sup>31</sup>P chemical resonances (δ 27.72, 27.68) in approximately equal intensities. (The available Supporting Information gives an expanded version of Table 5 at nine ratios of PhCH<sub>2</sub>Br/**8**.)

Comparisons of the two scavengers show that both PhSH and PhCH<sub>2</sub>Br in sufficient amounts reduce the yield of phosphonate **9** to 3–5%, which presumably corresponds to the yield from geminate radical pair combination. Interestingly, the required amount of PhCH<sub>2</sub>Br (PhCH<sub>2</sub>Br/**8** = 23–51) in all three solvents is much greater than the quantity of PhSH (PhSH/**8** = 0.5–1.0) needed to prevent the out-of-cage formation of phosphonate **9**. By contrast, phenylphosphonate, (**15**) undoubtedly formed via reaction of cage-escape phosphinoyl radicals (**6**) with benzene (Scheme 2), disappears at lower benzyl bromide concentrations (PhCH<sub>2</sub>Br/**8** = 7.4) than are required to minimize the yield of phosphonate **9** at 4–5% (PhCH<sub>2</sub>Br/**8** = 30). Indeed, as noted earlier, a 10% yield of phosphonate **15** persists at PhSH concentrations (PhSH/**8** = 5.7) much above those required to reduce the yield of **9** to the 3–5% range. These differences between the two scavengers are addressed in the Discussion section.

**TEMPO**. The addition of TEMPO in amounts similar to those for added thiophenol (TEMPO/**8** = 0.09–2.0) in cyclohexane causes the yield of **9** to level out at 4–5%, providing a third measure of the cage yield of **9** (Table 3). Concentrations of TEMPO were kept very low so as to minimize the “anti-scavenger” effect noted by Turro et al.<sup>16</sup> Simultaneously, the yields of (MeO)<sub>2</sub>P(O)H (**10**) and *p*-acetyl toluene (**12**) drop to zero. Radical coupling product **25** was isolated from photolysis of **8** in the presence of added TEMPO in acetonitrile solution and characterized by HRMS, and by comparison of its spectral properties to those previously reported for the benzyl analogue.<sup>17</sup> However, the formation of dimer **11** at the ratio TEMPO/**8** = 2.0 is not totally eliminated, though its accountability yield reduced from 12% to 2%. The photolysis of the benzyl analogue of trapping product **25** (formed by radical coupling) has been reported.<sup>17b</sup> Photolysis of **25** would yield *p*-acetylbenzyl radicals (**7a**) and provide a secondary pathway for reformation of dimer **11** under TEMPO-trapping conditions.



Furthermore, a peak at δ 6.7 in the <sup>31</sup>P NMR spectrum (CD<sub>3</sub>-CN) of the crude photolyzate is assigned to **26**. This is consistent



with the literature value for **27** (δ<sup>31</sup>P = 4.9, acetone-*d*<sub>6</sub>).<sup>18</sup> Attempts to isolate **26** by liquid chromatography failed. The

(16) Step, E. N.; Buchachenko, A. L.; Turrow, N. J. *J. Am. Chem. Soc.* **1994**, *116*, 5426.

(17) (a) Johnston, L. J.; Tencer, M.; Scaiano, J. C. *J. Org. Chem.* **1986**, *51*, 2806. (b) Korolenko, E. C.; Cozens, F. L.; Scaiano, J. C. *J. Phys. Chem.* **1995**, *99*, 14123.

(18) Busfield, W. K.; Grice, I. D.; Jenkins, I. D. *Aust. J. Chem.* **1995**, *48*, 625.

thermal instability of **26** precluded its study by GC/MS. Convincing evidence for the formation of **26** came from photolysis of di-*tert*-butyl peroxide in a solution of TEMPO in dimethyl phosphite (**10**). Observed in the  $^{31}\text{P}$  NMR spectrum of the crude products was a very predominant peak with chemical shift ( $\delta^{31}\text{P} = 6.1, \text{C}_6\text{D}_6$ ) close to that seen from the **8**/TEMPO photolysis. Undoubtedly, radical **6** is formed by *tert*-butoxy radical abstraction of hydrogen from **10** and is then trapped by TEMPO to form **26**. Indeed, **27** was previously prepared by the same approach.<sup>18</sup>

**Phosphite 1.** Both PhSH and benzyl bromide effectively scavenge radicals from photolysis of **8** that escape geminate combination (Tables 3–5). However, the necessary use of UV light of relatively short wavelengths (254 nm) for the photorearrangement of **1** results in the photolysis of added benzyl bromide.<sup>7</sup> Indeed, a control irradiation of an acetonitrile solution of benzyl bromide in the presence of  $(\text{MeO})_3\text{P}$  generated major amounts of phosphorobromidate **13**, presumably from reaction of bromine atoms with  $(\text{MeO})_3\text{P}$  and subsequent loss of methyl radical by  $\beta$  scission. Use of *tert*-BuBr, which is an effective scavenger<sup>15</sup> of phosphinoyl radical **6** formed on direct irradiation (>300 nm) of dimethyl 1-naphthylmethyl phosphite,<sup>19</sup> also is precluded by the appreciable UV absorption and reaction of *tert*-BuBr at 254 nm.

Unfortunately, phenyl mercaptan also is an inappropriate scavenger of radicals from **1** as it displays strong ultraviolet absorption at 254 nm. Likewise, TEMPO absorbs strongly at this wavelength.

**Benzene as Radical Scavenger in the Photorearrangement of 1.** Since solvent benzene was shown to be a very effective free-radical scavenger in the photolysis of **8** (Scheme 1), we looked for phosphonate **15** and products **22** and **23** on direct irradiation of **1** in benzene. Indeed, the formation (Table 2) of 1–2% of phenylphosphonate **15** was confirmed by GC/MS and quantitated by GC. Furthermore, the generation of **22**, **23a**, and **23b** in total amounts 1–2% (GC detection and quantitation) was indicated by  $^{31}\text{P}$  spectroscopy ( $\delta^{31}\text{P} = 30.79, 27.72, 27.68$ ) of the crude photolyzate. Products **23a** and **23b** were seen in near-equal amounts as estimated from their  $^{31}\text{P}$  NMR resonances at  $\delta$  27.22 and 27.68. (See Experimental Section and formation of these products on photolysis of **8** in the presence of benzyl bromide discussed earlier.)

**Quantum Yields for Photolysis of 1 and 8.** The quantum yields for the photoreactions of **1** (cyclohexane) and **8** (benzene), at 5–10% conversion of phosphite, were determined by irradiation at 266 nm (phosphite **1**) or 335 nm (phosphite **8**) with light from the high-pressure UV lamp of a PTI Quantacount electronic actinometer.<sup>20</sup> The quantum yield for formation of phosphonate **2** ( $\Phi_{\text{P}}$ ) is 0.43. For **8**  $\Phi_{\text{P}}$  is 0.074, while the quantum yields for both **11** and **15** formation are 0.11.<sup>21</sup> Taken together the total quantum yield for the three radical combination products **16**, **17a**, and **17b** is 0.18. (The quantum yields for formation of **11** are based on its chemical yield and not doubled to account for the stoichiometry of *p*-acetylbenzyl radical dimerization to give **11**.) The total quantum yield ( $\Sigma\Phi_i$ ) for all products accounted for from the photoirradiation of **8** is 0.47.

## Discussion

**Photolysis of Phosphite 8.** Phosphite **8**, an acetophenone derivative, is ideally set up for reaction via its triplet excited

state. (Indeed, its UV spectrum is closely similar to that of acetophenone.) The quantum yields for product formation indicate that photoreaction occurs quite efficiently ( $\Sigma\Phi_i = 0.47$ ). The low cage yield of phosphonate **9** (3–5%) is consistent with the initial formation of triplet radical pairs (**6** and **7a**, Ar = *p*-acetylphenyl), most of which undergo diffusion rather than combination. A fraction of them (4–8%) undergo nongeminate recombination as random free pairs to raise the total accountability yield of phosphonate **9** to 7–13%. As will be illustrated with examples later in the paper, the low percentage random recombination of **6** and **7a**, in which only one is a relatively stable species, is quite normal.

The cage-escape radicals **6** and **7a** (Ar = *p*-acetylphenyl) from photolysis of **8** are trapped by radical scavengers, PhSH and benzyl bromide (eqs 4, 6, 9), to yield phosphorobromidate **13**, phosphite **10**, *p*-acetylbenzyl (**12**) and cross-combination product **21**. With *PhCH\_2Br* as a scavenger in cyclohexane and acetonitrile (Table 4), the sum of the yields of dimer **11** and cross coupling product **21**, if stoichiometry is considered, account for 45–66% of the *p*-acetylbenzyl radical potentially formed from **8** (Table 4). Including phosphonate **9**, *p*-acetyl radical accountabilities are 52–82%. (The increase in yield of phosphonate **9** in acetonitrile and cyclohexane upon addition of benzyl bromide in relatively low concentrations ( $\text{PhCH}_2\text{Br}/\mathbf{8} \approx 0.5$ ) is not readily rationalized.) Similarly, in the presence of PhSH as a scavenger, *p*-acetylbenzyl accountabilities as high as 53% (benzene) attest to the large numbers of radical pairs generated by irradiation of phosphite **8**. Added TEMPO yields scavenging products **25** and **26** from interception of *p*-acetylbenzyl (**7a**) and phosphinoyl (**6**) radicals, respectively. Indeed, the good yields of radical trapping products with *PhCH\_2Br* and PhSH as scavengers confirm that the reaction involves formation of relatively long-lived, presumably triplet radical pairs (**6** and **7a**), and that geminate recombination to form phosphonate **9** is a minor pathway. All three radical scavengers point to a cage yield of phosphonate **9** of 3–5%.

The apparent 3–5% geminate recombination of initial pairs **6** and **7a** (Ar = *p*-acetylphenyl) to give phosphonate **9** potentially could include some product from rapid combination of singlet pairs formed from the singlet excited state of **8** in competition with singlet–triplet intersystem crossing. Benzophenone undergoes singlet–triplet intersystem crossing ( $k_{\text{ISC}} = 10^{10} \text{ s}^{-1}$ ) about ten times more rapidly than does acetophenone,<sup>22</sup> to which phosphite **8** is closely related. A study of the cage yield of the *p*-benzoylbenzylphosphonate, from irradiation of the benzophenone analogue of **8**, could be informative.

Benzene solvent itself is a scavenger of phosphinoyl radical **6**, as shown by the products formed (Scheme 2). This results in even higher accountabilities of radicals from the presumed triplet pair **6** and **7a** (Ar = *p*-acetylphenyl) in benzene compared to cyclohexane and acetonitrile, as seen in Table 1 and noted in the Results section. The trapping of key radicals from the photolysis of **8** in benzene will be discussed in more detail in later paragraphs.

It should be clearly noted that not one of the three scavengers (benzyl bromide, PhSH, or solvent benzene) that give identifiable, quantitated products by itself gives maximum accountabilities of both radicals **6** and **7a**. However, use of all three allows accountabilities of greater than 90% to be obtained for both radicals.

Scheme 2 is totally consistent with previously reported CIDEP<sup>6</sup> and  $^{31}\text{P}$  CIDNP<sup>5</sup> work on the photolysis of phosphite

(19) Ganapathy, S.; Soma Sekhar, B. B. V. Unpublished results from this laboratory.

(20) The quantum yield determinations were described previously.<sup>6</sup>

(21) Previously reported quantum yields for formation of **11** and **15**<sup>6</sup> have been corrected to reflect repeated determinations of product yields.

(22) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings Publishing: Menlo Park, CA, 1971; Chapter 8.

8. Thus, the predominance of initial triplet radical pairs was revealed by the E\*/A (enhanced emission) doublet pattern of the CIDEP spectrum for the phosphinoyl radical **6** from direct irradiation of **8**. For the *p*-acetylbenzyl radical, appropriate net emissive polarization was seen, on which was superimposed an E/A pattern.<sup>6</sup> Furthermore, <sup>31</sup>P CIDNP polarizations for products **10**, **13**, and **15–17** conformed to those expected from the reactions of initially formed triplet radicals.<sup>5</sup> A classic field effect on the sign of the polarization of (MeO)<sub>2</sub>P(O)Br (**13**), formed from radical **6** following its escape from the initial solvent cage, also was noted.<sup>6</sup>

**Photolysis of Phosphite 1.** By contrast to **8**, however, the product distribution from photo reaction of **1** reflects the predominant formation of the photo-Arbuzov product, phosphonate **2**, in high quantum efficiency ( $\Phi_P = 0.43$ ). Nonetheless, a small percentage yield (3–6%) of cage escape product bibenzyl (**20**) from dimerization of radical **7b** (Ar = Ph), eq 7, is noted. This corresponds to a 6–12% accountability (Table 2) of potentially formed benzyl radicals (**7b**). The 4–8% yield of dimethyl phosphite (**10**), detectable at higher conversions of **1** (see Results), probably arises from phosphinoyl radical **6** (eq 4). Suggestive of the formation of cage-free phosphinoyl radical **6** and its trapping by solvent benzene is the reduced yield of phosphonate **2** in benzene at 14% conversion of **1**, compared to its yield in the other two solvents. Both <sup>31</sup>P NMR and GC/MS confirmatory evidence for cage-free **6** is seen in the formation in benzene of phenylphosphonate **15** (1–2%), along with small amounts of products **22** and **23** (Scheme 2 with PhCH<sub>2</sub><sup>•</sup> (**7b**) in place of *p*-MeCOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub><sup>•</sup> (**7a**)).

On the basis of the relatively minor amount of radical diffusion that accompanies the photorearrangement of **1** to **2**, this process is most simply understood in terms of reaction via the singlet excited state of **1** to generate *singlet radical pairs 6 and 7b* (Ar = Ph). These pairs are relatively short-lived and, therefore, *primarily undergo geminate combination* to give photo-Arbuzov rearrangement product **2** [**1** → (**6**, **7b**) → **2**]. The failure to observe CIDEP or <sup>31</sup>CIDNP signals on direct irradiation of **1**<sup>23</sup> also is in accord with the postulation that the radical pairs involved are very short-lived. This is in contrast to the important CIDEP and <sup>31</sup>P CIDNP effects seen from the predominantly triplet pairs formed on direct irradiation of **8** or triplet-sensitized photoreaction of the 1-naphthylmethyl analogue of **1**.<sup>5,6,23</sup>

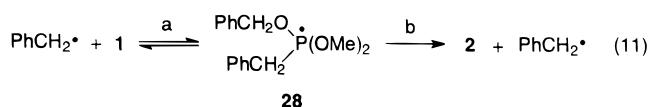
Further evidence for the formation of radical pairs in the direct photolysis of **1** and related phosphites comes from research from this laboratory on **3** and the analogue of phosphite **3** with a methyl substituent at the ring carbon next to oxygen.<sup>24</sup> The photo-Arbuzov rearrangement of essentially a single enantiomer of the diastereomer with ring methyl and 1-phenylethoxy ring substituents oriented in *cis* fashion was carried out. X-ray crystallography and <sup>31</sup>P NMR spectroscopy demonstrated that approximately 20% of the photo-Arbuzov product phosphonate was formed with inverted stereochemistry at the carbon stereogenic center of the 1-phenylethyl bonded to phosphorus.

A combination of concerted and free-radical pair pathways for the formation of **2** cannot be ruled out. However, there is no evidence for it. There remains as well the possibility that a very limited portion of the excited singlet of **1** undergoes intersystem crossing to the molecular triplet, followed by generation of triplet radical pairs that are at least in part responsible for the radical diffusion product bibenzyl (**20**) and

the products **15**, **22**, and **23** from addition of phosphinoyl radical **6** to benzene (Scheme 1 with radical **7b** in place of **7a**). However, we could not find a triplet quencher with suitable energetics and optical properties that was not also a radical trap.

The unsuitability of PhSH and the *tert*-butyl and benzyl bromides as scavengers of radical intermediates from photolysis of **1** is particularly disappointing as their use presumably would have further established the presence of cage-free radicals from irradiation of **1**. Thus, in results as yet unpublished,<sup>19</sup> the direct irradiation of 0.01-M solutions of a related phosphite, dimethyl 1-naphthylmethyl phosphite, was seen to yield the corresponding 1-naphthylmethylphosphonate in yields comparable to those for **2** seen in the present study. *As with phosphite 1, no CIDEP or <sup>31</sup>P CIDNP phenomena were observed.*<sup>23</sup> Scavengers give strong evidence for the formation of radical pairs. With the 1-naphthyl phosphite,<sup>19</sup> addition of *tert*-BuBr in increasing quantities reduced the accountability yields of phosphonate (15–17% conversions) from 71% to 61% in cyclohexane and from 74 to 69% in benzene. These reductions are accompanied by formation of 10–15% of (MeO)<sub>2</sub>P(O)Br (**13**). Added PhSH increases yields of **10** and 1-methylnaphthalene and reduces to zero the yield of the 1-naphthylmethyl radical dimer.

Finally, the possibility that phosphonate **2** arises via a chain reaction involving reaction of benzyl radicals with phosphite **1** via phosphoranyl radical **28** (eq 11) must be addressed. Contrary



evidence comes from the quantum yield for formation of **2** of less than one. Moreover, a crossover study, reported in our earlier communication,<sup>1</sup> excluded such a mechanism. Furthermore, in a recent paper<sup>25</sup> we reported the failure of benzyl radicals, formed on  $\beta$  scission of phosphoranyl radical [Et-(PhCH<sub>2</sub>O)P(OMe)<sub>2</sub>]<sup>•</sup>, to react with PhCH<sub>2</sub>OP(OMe)<sub>2</sub>. Benzyl radicals bond too weakly to phosphites (eq 11a) to generate **28**.

**Scavenging of Radical Pairs from 8 in Benzene by PhCH<sub>2</sub>Br.** In benzene at lower conversions of **8** in the absence of scavengers, as high as 56% of the phosphinoyl radicals (**6**) potentially formed are accounted for in products **9**, **15**, **16**, **17a**, and **17b** (Table 5). Likewise, if corrections are made for reaction stoichiometry, products **9**, **11**, **12**, **16**, **17a**, and **17b** account for up to 92% of theoretically formed radical **7a** (Ar = *p*-acetylphenyl). Clearly, benzene as solvent is a highly effective trap for radicals from **8**.

The product and radical scavenger studies in benzene are in general accord with and support the reactions of Scheme 1 and merit discussion in more detail. The absence of *p*-acetyltoluene (**12**) at a benzyl bromide/**8** ratio of 3.7/1 is accompanied by a large reduction, from 12 to 4.5%, in the yield of phenylphosphonate **15**. The latter product presumably is formed in the disproportionation reaction of **14** with **7a** that also generates **12** (Scheme 1). These results are consistent with much reduced formation of **14** when radical **6** is diverted by increasing amounts of PhCH<sub>2</sub>Br to form **13**. Further addition of benzyl bromide (benzyl bromide/**8** = 7.4, Table 5) brings the yield of phosphonate **15** to zero. At that concentration of benzyl bromide, the accountability of radical **6** as the phosphorobromidate (**13**) is 43%. Though phosphonate **15** is no longer detected at a PhCH<sub>2</sub>Br/**8** ratio of 7.4/1, the total yields of coupling products

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

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**16**, **17a** and **17b**, which also must arise from reaction of *p*-acetylbenzyl radical with **14**, still are 5–6% (Table 5). This is consistent with the dominance of coupling products **16**, **17a**, and **17b** (27% total) compared to **15** (16%) at 11% conversion of **8** in the absence of PhCH<sub>2</sub>Br (Table 1). Nonetheless, these products essentially disappear (<1% of each) at PhCH<sub>2</sub>Br/**8** ratios above 9.7/1, at which point the phosphonate **9** yield (5.3%) is close to the fully minimized 4.5% yield of **9** encountered at 30/1 and higher ratios of PhCH<sub>2</sub>Br/**8** (Table 5). At high PhCH<sub>2</sub>Br/**8** ratios (20/1–51/1), the accountability of **6**, as measured by formation of **13**, rises to 83–95%. The ratio of percentage yields of **11**/**21**/**20** at these ratios of PhCH<sub>2</sub>Br/**8** is about 16/26/12 (not corrected for stoichiometry of formation of **11** and **20**), reasonably close to the ratio expected for random combination of benzyl and *p*-acetylbenzyl radicals present in nearly equal concentrations.

The concentrations of benzyl bromide scavenger required to reduce the yield of phosphonate **9** to the 3–5% level (apparent cage yield), by trapping phosphinoyl radical **6**, are close to what might be predicted. Thus, the known rate constant for addition of (EtO)<sub>2</sub>P(O)• to benzene is  $2.9 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C<sup>9</sup> and for reaction with benzyl bromide is  $1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  at ambient temperature.<sup>15</sup> Both rate constants are presumably very close to those for radical **6** (eq 9 and formation of **14**, Scheme 2). Therefore, at 0.015 M concentration of benzyl bromide (PhCH<sub>2</sub>Br/**8** = 1) in solvent benzene (benzene ≈ 13 M), the addition of (C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>P(O)• to benzene can then be predicted to be about two times as rapid as abstraction of bromine from benzyl bromide. At a PhCH<sub>2</sub>Br/**8** ratio of (4–8)/1 (Table 4), the rate of trapping of **6** by benzyl bromide (eq 9) should be 2–4 times faster than its rate of addition to benzene. The accountability yield of phosphonate **9** is reduced to 7% at PhCH<sub>2</sub>Br/**8** = 8. A 20/1 ratio is required to decrease the yield of **9** to 5.3. Ratios greater than 25/1 bring the yield of **9** into the 3–5% range, in which all **6** that escape the solvent cage have been scavenged. At PhCH<sub>2</sub>Br/**8** = 25, the calculated ratio for the rate of bromine abstraction to that for addition to benzene is 12.

In keeping with Scheme 1, the formation of benzyl radicals in the PhCH<sub>2</sub>Br trapping experiments in benzene (eq 9) results in the generation (eq 7) of bibenzyl, **20**. Benzyl radicals also participate in the reactions of Scheme 2 to form the benzyl analogues of adducts **16**, **17a**, and **17b** and the products **22** and **23** (Table 5). As the PhCH<sub>2</sub>Br/**8** ratio is increased gradually from 0.5 to 7.4, the bibenzyl accountability yield (corrected for stoichiometry) increases accordingly from 4% to 34% (Table 5). In keeping with Scheme 1, the yields of cross dimer **21** rise from 10 to 26%. Perhaps surprisingly, the products **22** and **23** from benzyl radical trapping of **14** remain constant at 3–4% total yield up to a PhCH<sub>2</sub>Br/**8** ratio of 7.4 (Table 5).

**Scavenging by PhSH of Radical Pairs from Photolysis of 8 in Benzene and Other Solvents.** The amount of thiophenol required to scavenge all of the cage escape radicals **6** and **7a** (Ar = *p*-MeCOC<sub>6</sub>H<sub>4</sub>) in acetonitrile and cyclohexane and reduce the yield of phosphonate **9** to 3–5% is much less than the quantity of benzyl bromide required to have the same effect (Tables 3 and 4). This great a difference would not be expected if the primary reaction responsible for reduction of the yield of **9** is the trapping by PhSH of phosphinoyl radical **6** (eq 4). Indeed, on the basis of model reactions, PhSH should be the better trap for **6**, but only marginally so. Thus, for the related radical Ph<sub>2</sub>P(O)•, the rate constant for reaction with thiophenol

is  $1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  at  $23 \pm 2 \text{ °C}$ ,<sup>26</sup> while that for removal of bromine atom from benzyl bromide is smaller,  $5.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>27</sup> However, with PhSH the reduction in the yield of phosphonate **9** from combination of cage-free radicals **6** and **7a** (Ar = *p*-acetylphenyl) is the result of the simultaneous trapping of both **6** and **7a**. Indeed, at a PhSH/**8** ratio of only (0.25) in cyclohexane and acetonitrile, the yields of **11**, formed by dimerization cage-free *p*-acetylbenzyl radicals (**7a**), are greatly reduced with concomitant large increases in amounts of the trapping products **10** and **12**. The effect reaches a maximum at a PhSH/**8** ratio of 1.0 when all *p*-acetylbenzyl radicals are diverted to **12**. Indeed, it is the simultaneous removal of both the phosphinoyl (**10**) and *p*-acetylbenzyl (**7a**) radicals that is primarily responsible for the much greater efficiency of PhSH, compared to PhCH<sub>2</sub>Br, in reduction of the yield of **9** in cyclohexane and acetonitrile to the 3–5% level.

In benzene similar effects on the yields of phosphonate **9** are seen (Table 3), except that the scavenging of **6** by PhSH to form phosphite **10** at PhSH/**1** = 1 is less efficient than in cyclohexane and acetonitrile. This is revealed by the yield of **10** of only 12% and the remaining 20% yield of phenylphosphonate **15**, both of which incorporate the (MeO)<sub>2</sub>P(O)• radical (**6**), even though the yield of phosphonate **9** has been reduced to 3–4%. Thus, it would appear that the rate of abstraction of hydrogen from PhSH by phosphinoyl radical **6** is slower than its rate of addition to benzene to form **14** and the products derived from it. Unfortunately, the rate constant for abstraction of hydrogen from PhSH by (MeO)<sub>2</sub>P(O)• is not known. As noted in the previous paragraph, that for hydrogen abstraction by Ph<sub>2</sub>P(O)• is  $1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  at  $23 \pm 2 \text{ °C}$ .<sup>26</sup> This is only about 2.5 times greater than the rate constant ( $5.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) for abstraction of bromine from PhCH<sub>2</sub>Br by Ph<sub>2</sub>P(O)•. If the relative rate constants for (EtO)<sub>2</sub>P(O)• and Ph<sub>2</sub>P(O)• for reaction with PhSH and PhCH<sub>2</sub>Br are similar, then for (EtO)<sub>2</sub>P(O)• (and presumably (MeO)<sub>2</sub>P(O)•) the rate constant for abstraction from PhSH should be about 2.5 times the known rate constant<sup>15</sup> for reaction of (EtO)<sub>2</sub>P(O)• with PhCH<sub>2</sub>Br ( $1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) or  $3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . The pseudo first-order rate constants for formation of adduct **14** and abstraction by radical **6** of hydrogen from PhSH, at the concentrations of PhSH (0.015 M) and benzene (≈ 13 M) used, are calculated to be approximately equal ( $(4-5) \times 10^4 \text{ s}^{-1}$ ). Thus, the continued formation of phosphonate **15** via adduct **14** at PhSH/**8** = 1.0 ([PhSH] = 0.015 M) and above, in competition with the trapping of phosphinoyl radical **6** by its conversion to phosphite **10**, is not surprising. All *p*-acetylbenzyl radicals (**7a**) are scavenged as *p*-acetyltoluene (**12**) at PhSH/**8** = 1 and below to turn off the formation of phosphonate **9** by random encounter of radicals **6** and **7a** (Ar = *p*-acetylphenyl). This, along with the formation of **14**, reduces the yield of **9** to 3%.

Adduct **14** may indeed be trapped by disproportionation with phenylthiyl radicals to give **15** directly and perhaps also by abstraction of hydrogen from PhSH to form the cyclohexadiene product which is subsequently aromatized to **15**. The high efficiency of modest concentrations of PhSH in benzene in reducing the formation of phosphonate **9** results primarily from its trapping of the *p*-acetylbenzyl radical (**7a**) and only secondarily from its interception of radical **6**. In this way the inefficiency of PhSH in reducing the yield of phenylphosphonate **15** is readily understood. If in fact the formation of **14** is

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reversible, the puzzling increase in yield of **15** encountered on addition of PhSH is also explained.

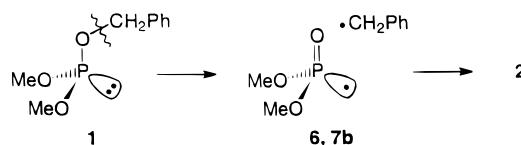
**Energetics of Radical Pair Formation.** Benzyl excited singlets clearly possess enough energy to cleave the benzylic C–O bond in **1** to form an intermediate radical pair (**6** and **7b**, Ar = C<sub>6</sub>H<sub>5</sub>). Thus, the singlet energy for benzyl alcohol, a reasonable model for **1**, is 107 kcal/mol in nonpolar solvents.<sup>28</sup> The bond dissociation energy for the carbon–oxygen bond of benzyl alcohol (77 kcal/mol)<sup>29</sup> represents a likely value for that of the *simple cleavage* of the benzyl–oxygen bond of PhCH<sub>2</sub>–OP(OMe)<sub>2</sub> (**1**). However, the cleavage of the C–O bond in **8** evidently occurs via the triplet state with an energy presumably only about that for triplet acetophenone, 72 kcal/mol.<sup>30</sup> The formation of product **2** from **1** is at least 25 kcal/mol exothermic.<sup>31</sup> This is a result of the formation of the phosphoryl  $\pi$  bond since the phosphorus–carbon bond formed in **2** is weaker than phosphorus–oxygen bonds broken in **1**. It seems likely, therefore, that carbon–oxygen bond scission in excited triplet **8** is assisted by partial phosphorus oxygen  $\pi$  bond formation in the transition state for generation of phosphinoyl radical **6**. (That is, the benzylic bond dissociation energy is less than the 77 kcal/mol value<sup>29</sup> for PhCH<sub>2</sub>OH). The previously reported generation of triplet pair **6**, **7** (Ar = 1-naphthyl) from the triplet excited state of dimethyl 1-naphthylmethyl phosphite,<sup>6</sup> which is presumably close in energy to that of 1-methylnaphthalene (59.6 kcal/mol),<sup>32</sup> most assuredly is assisted by rehybridization about phosphorus in the transition state for C–O cleavage (results to be published).

**Comparisons with Related Radical-Pair Forming Reactions.** The formation and reactions of geminate free-radical pairs by thermal and photochemical means has been studied extensively.<sup>33</sup> As noted in the Introduction, there is considerable current interest<sup>7</sup> in the mechanisms of photolysis of arylmethyl and diarylmethyl systems, ArCH<sub>2</sub>-Z and Ar<sub>2</sub>CH-Z, for example where Z is a halogen.<sup>7c,f,g</sup> This applies as well to esters, ArCH<sub>2</sub>–OCOR, with, e.g., Ar = phenyl and 1-naphthyl and R = CH<sub>3</sub> or Bu-*tert*.<sup>7a,b</sup> Photolysis of the halides and esters gives products of both radical pairs and ion pairs, depending on solvent and substituents in the aryl rings.<sup>7</sup> Unlike phosphite **8**, the esters cannot be caused to react from the triplet excited state.<sup>7a</sup> However, the photolyses of the halides can be induced by interaction with triplet sensitizers.<sup>7a,d,f,g</sup> For the esters it is proposed that on direct irradiation, radical pairs are formed initially, followed by electron transfer to form ion pairs in competition with decarboxylation.<sup>7a,b</sup> Diphenylmethyl chloride photolysis evidently initially forms both ion and radical pairs.<sup>7c</sup>

The studies of **1** and **8** reported here have not directly addressed the possibility of formation of ion pairs. Nevertheless, the similar amounts of phosphorobromidate **13** generated on trapping of radical **6** in polar and nonpolar solvents argues against the formation of ion pairs following intersystem crossing of the radical pairs (**6,7a**) generated from **8**. The failure of the

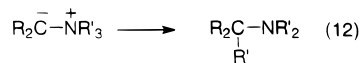
yield of phosphonate **9** to vary with solvent polarity also speaks against ion pair intermediates from **8**. Studies of the effects of ring substituents on the direct photolysis of **1**, and the failure to find products of ion pairs in the presence of added MeOH, will be reported in a subsequent publication on photolyses of ring-substituted benzyl and 1-naphthylmethyl phosphites.<sup>34</sup>

The photolysis of **1** via presumed *singlet* free radical pairs (**6,7b**) is characterized by 60–80% cage combination. This assumes that random radicals formed by diffusion from the solvent cage undergo very little return, as was confirmed for those from **8**. It is significant that the radical pair **6,7b** is formed without an intervening molecule such as nitrogen or carbon dioxide that is commonly formed,<sup>33b</sup> for example, on thermolysis of azo compounds, R–N=N–R, and *tert*-butyl peresters, RCO<sub>2</sub>–O–Bu-*tert*. Thus, the pair **6**, **7b** is similar to the so-called *proximate radical pairs*<sup>35</sup> postulated in the thermal rearrangements of the chiral ketenimine Ph<sub>2</sub>C=C=NCHPhMe to Ph<sub>2</sub>C(CN)–CHPhMe. The singlet radical pairs formed evidently couple very rapidly, as they give high yields of product and greatly increased retention of configuration compared to their azo counterparts, for example PhCH<sub>2</sub>–N=N–CHPhMe,<sup>36</sup> and MePhCh–N=N–CHPhMe.<sup>37</sup> The radical centers in the singlet pair **6,7b** combine with retention of configuration at phosphorus.



Photocleavage of the C–O bond, oriented as shown below to optimize the anomeric interaction of the phosphorus lone pair with the O–C antibonding orbital (anomeric effect), would require the radicals so formed to undergo very little motion prior to coupling.

The photo-Arbuzov rearrangement of **1** is also mechanistically reminiscent of the thermal Stevens rearrangement (eq 11), found to proceed largely intramolecularly and at least in part via radical pairs.<sup>38</sup> Furthermore, the photo-Fries rearrangements of phenyl and 1- and 2-naphthyl acetates give CIDNP phenomena as evidence for radical pair intermediates that undergo largely geminate recombination.<sup>39</sup>



The inefficiency of coupling of random phosphinoyl (**6**) and *p*-acetylbenzyl (**7a**) radicals that results in the low yields of phosphonate **9** found in the photolysis of **8** is not surprising on consideration of other radical pair systems. Thus, the ether *sec*-BuO–Bu-*tert* is not formed from the thermolysis of *sec*-BuCO<sub>2</sub>–O–Bu-*tert* which generates the geminate and then random pair

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*sec*-BuO<sup>•</sup>/*tert*-Bu<sup>•</sup>, initially separated by a CO<sub>2</sub> molecule.<sup>40</sup> Furthermore, the Norrish Type I photoreaction of optically active PhCOCHPhMe, to form triplet geminate pairs,<sup>41</sup> evidently features only about 4% recombination of random, cage-free benzoyl and 2-phenylethyl radicals. Higher yields of random combination are typically found only with more stable radicals,<sup>33</sup> as noted in the accountabilities of bibenzyl (**20**) and *p*-acetylbenzyl radical dimer (**11**).

**Potential Effect of Large Phosphorus Hyperfine Splitting Constant of Radical 6.** The phosphinoyl radical (MeO)<sub>2</sub>P(O)<sup>•</sup> **6** features a phosphorus hyperfine splitting constant of approximately 700 G.<sup>5,6</sup> A potential consequence could be a rapid hyperfine-induced intersystem crossing of the radical pairs formed from **1** and **8**. However, a consequent large increase in combination of geminate pair **6,7a** to give large amounts of phosphonate **9** clearly is not observed. This is despite the strong field-dependent effect of the large hyperfine splitting on the identity of the triplet pair formed.<sup>5</sup>

**Conclusions.** The photoreactions of phosphites **1** and **8** proceed with high efficiencies as shown by the quantum yields of product formation. The products of direct irradiation of phosphite **8** are accounted for by the proposal that **8** reacts primarily through its *triplet* excited state to generate relatively long-lived *triplet* radical pairs (**6** and **7a**, Ar = *p*-acetylphenyl). Consequently, the photo-Arbuzov product, phosphonate **9**, is formed in small amounts along with major quantities of radical diffusion products that are trapped by radical scavengers (solvent benzene, PhSH, PhCH<sub>2</sub>Br, and TEMPO). The apparent cage yield of **9** is 3–5%. The contrasting, relatively high yield of photo-Arbuzov phosphonate **2**, formed on direct irradiation of **1**, is indicative of the reaction of **1** largely via the *singlet* excited state. The formation of small amounts of both radical products and those from scavenging by benzene of radicals from **1** suggest that its photolysis, like that of **8**, proceeds via radical pairs that are *singlet*, not *triplet*, in nature and largely recombine. However, the possibility that phosphite **1** reacts in part following intersystem crossing of its *singlet* excited state to the *triplet*, which generates *triplet* radical pairs, cannot be ruled out.

## Experimental Section

**Materials.** Bibenzyl (**20**) (Aldrich), 4,4'-diacetylbibenzyl (**11**) (Trans World Chemicals), *p*-acetyltoylene (**12**) (Aldrich), *N*-bromosuccinimide (Janssen), PhSSPh (Aldrich), trimethyl phosphite (Aldrich), sodium benzenesulfinate acid (Aldrich), TEMPO (Aldrich), and *di-tert*-butyl peroxide (Aldrich) were used as received. Solvents were dried and argon saturated prior to use in photolysis. Benzene (Photorex reagent, Baker) was distilled from sodium. Acetonitrile and cyclohexane (Mallinckrodt, SpectrAR) were distilled from CaH<sub>2</sub> before use in the photochemical work. Thiophenol (PhSH, Aldrich) was distilled from calcium sulfate. Benzyl bromide (Aldrich), dimethyl phosphite (**10**) (Aldrich), benzyl alcohol (Aldrich), and dimethyl phenylphosphonate (**15**) (TCI) were distilled before use. Benzyl dimethyl phosphite (**1**),<sup>25</sup> dimethyl phosphorobromidate (**13**),<sup>42</sup> and dimethyl *N,N*-diethylaminophosphoramidate<sup>43</sup> were prepared by literature procedures.

**General Information.** Melting points (Thomas-Hoover melting point apparatus) are uncorrected. Unless stated otherwise, distillations of products were performed using a short path apparatus. Thin-layer chromatography (TLC) analyses were performed on EM silica gel 60

F<sub>254</sub> plates. Column chromatography was conducted on Merck silica gel (230–400 mesh) from EM Science. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA. High-performance liquid chromatographic (HPLC) separations of products were performed under isocratic conditions with a Waters 590 solvent delivery system, equipped with an ISCO V<sup>4</sup> UV Absorbance detector, using a 10 mm ID semipreparative, or a 21.4 mm ID preparative Dynamax HPLC column (100 Å spherical microsorb SiO<sub>2</sub> packing, 5 mm particle size, Rainin Instrument Co, Inc.).

NMR spectra were recorded on Varian NMR spectrometers (models XL 300B, Unity 300, and VXR 500). <sup>1</sup>H and <sup>13</sup>C chemical shifts are reported in δ ppm downfield from internal TMS. Coupling constants are in Hertz (Hz) and, if not otherwise noted, are proton–proton couplings. Phosphoric acid (85%) was used as external reference for the <sup>31</sup>P spectra. Mass spectra were recorded on a Finnigan MAT 95 mass spectrometer (EI, 70 eV) mode. GC/MS was run on a Hewlett-Packard Model 5890A series II gas chromatograph coupled to a Hewlett-Packard 5971A mass selective detector (MSD) operated in the EI mode. Inlet column was a DB-1 capillary (1% methyl silicone, J & W Scientific), size 30 M X 0.25 μm. HRMS spectra were obtained in the EI or CI (DB-210 capillary column) mode on a Finnigan Mat 95 High-Resolution Gas Chromatography/Mass Spectrometer with a Finnigan MAT ICIS II operating system. Masses are recorded in atomic mass units (*m/z*). GC analyses were performed on an HP 5890 series II gas chromatograph in the FID mode on a DB-1 (1% methyl silicone, J & W Scientific) capillary column (30 M X 0.25 μm). Quantitative GC analyses utilized tri-*n*-butyl phosphate as an internal standard against which all peaks were calibrated for sensitivity (response factor), except as otherwise noted. Ultraviolet spectra were obtained on a Hewlett-Packard 8452A diode array instrument. Wavelengths are reported in nm with extinction coefficients ε in M<sup>-1</sup>cm<sup>-1</sup>. UV data for **1** (CH<sub>3</sub>CN): λ<sub>max</sub>(ε) 252 (151), 258 (185), 264 (145); λ(ε) 280 (1.5), 300 (0.8). UV data for **8** (CH<sub>3</sub>CN): λ<sub>max</sub>(ε) 248 (15,780), 280 (1,242), 316 (71); λ(ε) 340 (38).

**Quantum Yields.** Determination of quantum yields for the photoreaction of **8** and other phosphites by use of a Quantacount Instrument, manufactured by Photon Technology, International, was described earlier.<sup>6</sup>

**Photolysis of Benzyl Dimethyl Phosphite (1) in Cyclohexane and Acetonitrile.** Stock solutions containing **1** (0.010–0.012 M) and tri-*n*-butyl phosphate (0.003 M) were prepared in argon-saturated solvents in a glovebag filled with argon. Portions (2 × 5 mL) of the solution were transferred into two quartz tubes and capped with an airtight septum. The solutions were purged with a slow stream of argon (10 min) and photolyzed at 24–26 °C at 254 nm in a Rayonet reactor. The reaction was monitored over time by GLC analysis. Products were identified by co-injection with authentic compounds and by GC/MS analysis. Product accountability yields, utilizing predetermined response factors, were based on phosphite converted. Pertinent data are given in Table 2.

**Photolysis of Benzyl Dimethyl Phosphite (1) in Benzene.** In addition to the products formed in cyclohexane and acetonitrile, minor amounts of phosphonate **15** as well as **22**, **23a**, and **23b** are generated. The latter three products were identified and quantitated as noted below in connection with the photolysis of phosphite **8** in benzene with added benzyl bromide trap.

**Photolysis of *p*-Acetylbenzyl Dimethyl Phosphite (8).** Stock solutions containing **8** (0.016–0.030 M) and internal standard (0.003 M) were prepared in the respective argon-saturated solvents in an argon glovebag. Portions (2 × 9 mL) of the solution were transferred into two Pyrex tubes, septum capped, argon purged (10 min), placed in a water bath at about 26 °C, and irradiated with light from a 450-W Hanovia medium-pressure mercury vapor lamp filtered through a uranium filter sleeve. The progress of the reaction was monitored by GLC analysis. Products were identified by co-injection with authentic samples and by GC/MS analysis. Accountability yields and other pertinent data appear in Table 1.

**General Procedure for the Photolysis of 8 in the Presence of Radical Traps.** Solutions (5 mL) containing **8** (0.014 M–0.018 M) and internal standard (0.003 M), with varying amounts of added radical traps, were prepared as described above for photolyses of **8** and

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irradiated with a light from a 450-W Hanovia medium-pressure mercury vapor lamp filtered through a uranium glass filter sleeve in a water bath at room temperature to 16–18% conversions of **8**. Reactions were monitored by GC during irradiation (450-W Hanovia medium-pressure lamp, uranium filter). Pertinent results are given in Tables 3–5.

#### Preparative Photolysis of *p*-Acetylbenzyl Dimethyl Phosphite (**8**).

A solution of phosphite **8** (0.125 g, 0.52 mmol) in deoxygenated, argon-saturated benzene (100 mL) was irradiated as described previously (450 W medium-pressure Hanovia, uranium glass filter). Progress of the reaction was monitored by GC analysis and the irradiation was discontinued (80 min) after 90% consumption of **8**.  $^{31}\text{P}$  spectrum ( $\text{C}_6\text{D}_6$ ) of the photolyzate displayed signals at  $\delta$  29.97, 27.83, 26.30, 25.97 and 21.64. The peaks at  $\delta$  27.83 and 21.64 correspond to **9** and **15**, respectively. The GC and GC/MS analysis of the photolyzate showed three unidentifiable peaks with  $\text{M}^+$  320 showing the nearly identical pattern. The peak at  $\delta$  29.97 was assigned to the adduct **16**, which was isolated, and the spectral data are given below. However, the remaining unidentifiable  $^{31}\text{P}$  NMR peaks at 26.30 and 25.97 can be assigned to **17a** and **17b**, although we have no evidence as to which is the *trans* isomer and which is the *cis* form. The photolyzate was concentrated and flash chromatographed on a silica gel column, eluting with 4% methanol:dichloromethane (monitored by GC). The polar products were collected and further purified by repeated HPLC chromatographic separations to furnish **16** (10.8 mg, 6.5%) and **18** (14.7 mg, 8.9%). During the isolation procedure, the unstable cyclohexadiene products **17a** and **17b** were aromatized to **18**. Spectral data for **16**:  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 121 MHz):  $\delta$  31.69.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz):  $\delta$  7.70 (d, 2 H,  $J = 8.0$  Hz), 6.91 (d, 2 H,  $J = 8.0$  Hz), 5.79 (m, 1 H), 5.68 (m, 1 H), 5.59 (m, 1 H), 5.45 (m, 1 H), 3.31 (d, 3 H,  $^3J_{\text{POCH}} = 10.7$  Hz), 3.29 (d, 3 H,  $^3J_{\text{POCH}} = 10.7$  Hz), 3.04 (dddd, 1 H,  $J_{\text{HH}} = 2.4$ , 5.8, 7.2, 8.3 Hz;  $^3J_{\text{PH}} = 21.7$  Hz), 2.62 (dddd, 1 H,  $J_{\text{HH}} = 1.5$ , 2.7, 5.6 Hz;  $^2J_{\text{PH}} = 29.6$  Hz), 2.54 (dd, 1 H,  $J_{\text{HH}} = 7.2$ , 13.4 Hz), 2.46 (dd, 1 H,  $J_{\text{HH}} = 8.3$  Hz, 13.4 Hz), 2.07 (s, 3 H).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 125.8 MHz):  $\delta$  197.44, 144.55, 135.80, 129.74, 128.91 (d,  $^2J_{\text{PC}} = 5.8$  Hz), 128.57, 125.90 (d,  $^2J_{\text{PC}} = 12.8$  Hz), 122.89 (d,  $^4J_{\text{PC}} = 6.2$  Hz), 119.20 (d,  $^3J_{\text{PC}} = 12.4$  Hz), 53.02 (d,  $^2J_{\text{POC}} = 7.0$  Hz), 52.86 (d,  $^2J_{\text{POC}} = 7.0$  Hz), 39.80 (d,  $^3J_{\text{PC}} = 24.0$  Hz), 36.32 (d,  $^1J_{\text{PC}} = 133.6$  Hz), 33.90 (d,  $^2J_{\text{PC}} = 4.1$  Hz), 26.54. MS (EI)  $m/z$  (rel intensity): 320 ( $\text{M}^+$ , 1), 319 (0.41), 318 (2.02), 211 (19.2), 187 (100), 165 (2.87), 155 (13.2), 109 (44.3). HRMS (EI)  $m/z$  ( $\text{M}^+$ ): calcd 320.1177, obsd 320.1156. For **18**:  $^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 121 MHz):  $\delta$  23.66.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 500 MHz):  $\delta$  7.88 (d, 2 H,  $J = 8.2$  Hz), 7.70 (dd, 2 H,  $J_{\text{HH}} = 8.2$  Hz,  $^3J_{\text{PH}} = 13.0$  Hz), 7.32 (dd, 2 H,  $J_{\text{HH}} = 8.2$  Hz,  $J_{\text{PH}} = 4.0$  Hz), 7.29 (d, 2 H,  $J = 8.2$  Hz), 4.09 (s, 2 H), 3.70 (d, 6 H,  $^3J_{\text{POCH}} = 10.1$  Hz), 2.55 (s, 3 H).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 125.8 MHz):  $\delta$  197.87, 146.20, 145.81 (d,  $^4J_{\text{PC}} = 2.9$  Hz), 136.13, 132.67 (d,  $^2J_{\text{PC}} = 10.5$  Hz), 129.67 (d,  $^3J_{\text{PC}} = 15.8$  Hz), 129.14, 125.82 (d,  $^1J_{\text{PC}} = 189.9$  Hz), 53.07 (d,  $^2J_{\text{POC}} = 5.7$  Hz), 42.31, 26.96. MS (EI)  $m/z$  (rel intensity): 318 ( $\text{M}^+$ , 33), 303 (100), 276 (2.5), 209 (2.7), 165 (14.4), 109 (2.1). HRMS (EI)  $m/z$  ( $\text{M}^+$ ): calcd 318.1021, obsd 318.1018. For **17a** or **17b**:  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ , 121 MHz):  $\delta$  26.30 or 25.97. GC/MS (EI)  $m/z$  (rel intensity) (shorter GC retention time): 320 ( $\text{M}^+$ , 1), 318 (2), 187 (100), 155 (19), 133 (5), 127 (17), 109 (70). GC–HRMS (CI)  $m/z$  ( $\text{M}^+ + \text{H}$ ): calcd for  $\text{C}_{17}\text{H}_{22}\text{O}_4\text{P}$  321.1256, found 321.1257. For **17a** or **17b**:  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ , 121 MHz):  $\delta$  26.30 or 25.97. GC/MS (EI)  $m/z$  (rel intensity) (longer GC retention time): 320 ( $\text{M}^+$ , 1), 319 (2), 187 (100), 155 (20), 133 (5), 127 (14), 109 (68). GC–HRMS (CI)  $m/z$  ( $\text{M}^+ + \text{H}$ ): calcd for  $\text{C}_{17}\text{H}_{22}\text{O}_4\text{P}$  321.1256, obsd 321.1254.

#### Products in the Photolysis of **8** in Benzene with $\text{PhCH}_2\text{Br}$ added.

For photolyses in benzene with added  $\text{PhCH}_2\text{Br}$ /**8** in the range 0.5–7.4, the crude photolyzate was examined by  $^{31}\text{P}$  NMR spectroscopy. In addition to the products observed on photolysis of **8** in benzene in the absence of benzyl bromide, a product peak at  $\delta$  28.8 corresponding to benzylphosphonate **2** was noted and also identified by GC. In addition new resonances at  $\delta$  30.79, 27.72, and 27.68, analogous to those for **16**, **17a**, and **17b**, reported above, were noted and assigned to the structures **22**, **23a**, and **23b**. Unlike **17a** and **17b**, the *cis* and *trans* isomers, **23a** and **23b**, were not separable by GC. The amounts of **22** and **23a/23b** were quantitated using the sensitivity factor for **16**. For **22** or **23a/23b** GC/MS (EI)  $m/z$  (rel intensity): 278 ( $\text{M}^+$ , 1), 277 (1), 188 (9), 187 (100), 156 (2), 155 (21), 110 (4), 109 (93), 92 (6), 91

(51); 278 ( $\text{M}^+$ , 1), 277 (2), 188 (9), 187 (100), 156 (2), 155 (21), 110 (8), 109 (95), 92 (13), 91 (49).

**Preparation of Dimethyl Benzylphosphonate (2).** Benzyl bromide (4.0 g, 23.4 mmol) and trimethyl phosphite (17.4 g, 140 mmol) were refluxed under argon at 110 °C for 2 h. The reaction mixture was concentrated in vacuo and dried under high vacuum. The crude residue was purified by distillation (bp 70 °C, 0.5 mmHg) to furnish **2** (3.04 g, 15.2 mmol, 65%).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 121 MHz):  $\delta$  29.44.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.23 (br s, 5 H), 3.59 (d, 6 H,  $^3J_{\text{POCH}} = 11.0$  Hz), 3.09 (d, 2 H,  $^2J_{\text{PH}} = 21.7$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  131.16 (d,  $^2J_{\text{PC}} = 9.6$  Hz), 129.65 (d,  $^3J_{\text{PC}} = 6.6$  Hz), 128.59 (d,  $^4J_{\text{PC}} = 3.0$  Hz), 126.94 ( $^5J_{\text{PC}} = 3.5$  Hz), 52.83 ( $^2J_{\text{POC}} = 7.1$  Hz), 32.76 ( $^1J_{\text{PC}} = 138.0$  Hz). MS (EI)  $m/z$  (rel intensity): 200 ( $\text{M}^+$ , 100), 104 (51), 91 (100). HRMS (EI)  $m/z$  ( $\text{M}^+$ ): calcd 200.0602, obsd 200.0678.

**Preparation of *p*-Acetylbenzyl Bromide.** *p*-Acetyltoluene (**12**) (83.0 g, 618 mmol), *N*-bromosuccinimide (132.0 g, 743 mmol), and benzoyl peroxide (250 mg) were dissolved in 1000 mL of benzene. The solution was purged with nitrogen for 10 min and stoppered. The solution was stirred vigorously during irradiation for 6 h with light from a 450-W Hanovia medium-pressure mercury lamp. The photolyzate was filtered, and the filtrate was washed with water. The organic layer was washed with saturated  $\text{NaHCO}_3$  solution, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated. To the concentrate anhydrous  $\text{K}_2\text{CO}_3$  (100 mg) was added. Distillation (bp 115 °C, 0.5 mmHg) afforded 63.2 g (48%) of the desired product, mp 42–43 °C (lit. 38–39 °C).<sup>44</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.94 (d, 2 H,  $J = 8.3$  Hz), 7.45 (d, 2 H,  $J = 8.3$  Hz), 4.48 (s, 2 H), 2.57 (s, 3 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz): 197.49, 142.87, 136.89, 129.33, 128.91, 32.31, 26.79.

**Preparation of *p*-Acetylbenzyl Alcohol.** *p*-Acetylbenzyl bromide (25.0 g, 117 mmol) and  $\text{CaCO}_3$  (63.0 g, 630 mmol) were added to dioxane–water (1:1, 720 mL). This reaction mixture was stirred at reflux for 15 h and then reduced in volume under vacuum. To the stirred mixture of the concentrate in  $\text{CH}_2\text{Cl}_2$  (500 mL) was slowly added dilute aqueous HCl until the solid material was dissolved in the water layer. The separated organic layer was washed with  $\text{Na}_2\text{CO}_3$ , dried over  $\text{Na}_2\text{SO}_4$ , and concentrated to a viscous oil. Crystallization of the concentrate from ether:pentane at –20 °C provided fine white crystals of the desired product (12.0 g, 60%), mp 53 °C (lit. 54 °C).<sup>45</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.90 (d, 2 H,  $J = 8.3$  Hz), 7.42 (d, 2 H,  $J = 8.5$  Hz), 4.74 (s, 2 H), 3.04–2.73 (br s, 1 H), 2.57 (s, 3 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  198.41, 146.61, 136.28, 128.73, 126.73, 64.57, 26.80.

**Preparation of *p*-Acetylbenzyl Dimethyl Phosphite (8).** A solution of *p*-acetylbenzyl alcohol (2.75 g, 18.3 mmol) and 1-*H*-tetrazole (0.75 g, 10.5 mmol) in freshly distilled acetonitrile was stirred under argon. Neat dimethyl *N,N*-diethylaminophosphoramidite (9.0 g, 54.5 mmol) was added dropwise at room temperature over a 5-min period. The reaction was stirred for 18 h at room temperature. Solvent removal under vacuum gave a solid material that was dissolved in dry pentane (75 mL), stirred for 5 min, and then allowed to settle. The supernatant liquid was cannulated under argon into a flask by Schlenk techniques. Solvent was removed from the stirred solution under vacuum. The crude residue was transferred to a molecular distillation apparatus in an argon glovebag. Distillation (oil bath temp. 75 °C, 0.025 mmHg) provided **8** (3.81 g, 86%) in 98% purity (GC).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 121 MHz):  $\delta$  141.25.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.95 (d, 2 H,  $J = 8.3$  Hz), 7.45 (d, 2 H,  $J = 8.3$  Hz), 4.92 (d, 2 H,  $^3J_{\text{POCH}} = 7.8$  Hz), 3.53 (d, 6 H,  $^3J_{\text{POCH}} = 10.9$  Hz), 2.60 (s, 3 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  197.92, 143.84 (d,  $^3J_{\text{PC}} = 4.5$  Hz), 136.60, 128.71, 127.30, 63.37 (d,  $^2J_{\text{POC}} = 11.1$  Hz), 49.59 (d,  $^2J_{\text{POC}} = 11.1$  Hz), 26.85. HRMS (EI)  $m/z$  ( $\text{M}^+$ ): calcd 242.0708, obsd 242.0709. Anal. Calcd for  $\text{C}_{11}\text{H}_{15}\text{O}_4\text{P}$ : C, 54.54; H, 6.25. Found: C, 54.20; H, 6.17.

**Preparation of Dimethyl *p*-Acetylbenzylphosphonate (9).** *p*-Acetylbenzyl bromide (9.0 g, 42.2 mmol) and trimethyl phosphite (36.0 g, 290 mmol) were refluxed under argon at 110 °C for 2 h. Solvent removal yielded a solid residue that was dried under high vacuum. Recrystallization from methanol:ether afforded pale yellow crystals of **9** (6.31 g, 62%), mp 64–66 °C.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 121 MHz):  $\delta$  28.22.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.88 (d, 2 H,  $J = 7.6$  Hz), 7.36 (d, 2

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H,  $J = 8.1$  Hz), 3.65 (d, 6 H,  $^3J_{\text{POCH}} = 10.9$  Hz), 3.19 (d, 2 H,  $^2J_{\text{PH}} = 22.2$  Hz), 2.55 (s, 3 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  197.72, 137.09 (d,  $^2J_{\text{PC}} = 9.1$  Hz), 135.95 (d,  $^5J_{\text{PC}} = 3.5$  Hz), 130.04 (d,  $^3J_{\text{PC}} = 6.0$  Hz), 128.77 ( $^4J_{\text{PC}} = 3.0$  Hz), 53.09 ( $^2J_{\text{POC}} = 7.1$  Hz), 33.12 ( $^1J_{\text{PC}} = 137.5$  Hz), 26.72. MS (EI)  $m/z$  (rel intensity): 242 ( $\text{M}^+$ , 19), 227 (100). HRMS (EI)  $m/z$  ( $\text{M}^+$ ): calcd 242.0708, obsd 242.0707. Anal. Calcd for  $\text{C}_{11}\text{H}_{14}\text{O}_4\text{P}$ : C, 54.54; H, 6.25. Found: C, 54.60; H, 6.23.

**Photolysis of 8 with TEMPO as a Trap.** Phosphite **8** (45.0 mg, 0.185 mmol) and TEMPO (30.0 mg, 0.192 mmol) were dissolved in 1.2 mL of degassed  $\text{CD}_3\text{CN}$  and irradiated in a flame-sealed quartz NMR tube to approximately 30% consumption ( $^{31}\text{P}$  NMR) of the phosphite under conditions such as those described previously for the photolysis of **8**. In addition to the peaks normally observed, the  $^{31}\text{P}$  NMR spectrum displayed a predominant peak at  $\delta$  6.67 that was assigned to **26**, formed by TEMPO trapping the phosphinoyl radical.

**Photolysis of Dimethyl Phosphite/di-tert-Butyl Peroxide/TEMPO Solution.** A solution of dimethyl phosphite (59.9 mg, 0.544 mmol), TEMPO (70.9 mg, 0.454 mmol) and di-*tert*-butylperoxide (0.08 mL, 63.6 mg, 0.435 mmol) in a 5-mL dry Pyrex tube was capped with airtight septum, argon purged for 5 min, and then irradiated with light from a 450-W Hanovia medium-pressure mercury vapor lamp. The progress of the reaction was monitored by  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ ), which displayed a predominant peak at  $\delta$  6.07, corresponding to **26**. Attempted purification of the photolyzate on silica gel column chromatography failed to isolate compound **26**.

**Isolation of 25 from the Photolysis of 8 in the Presence of TEMPO.** A solution of phosphite **8** (132 mg, 0.545 mmol) and TEMPO (88.0 mg, 0.563 mmol) in acetonitrile (30 mL prepared using the glovebag techniques described above) was irradiated as before (450 W Hanovia lamp, uranium glass filter). At 70% conversion of **8** (GC), irradiation was discontinued. The product solution was concentrated and then subjected to silica gel column chromatography. Elution with the 5% ethyl acetate:hexane, first fraction, was collected, concentrated,

and checked by  $^1\text{H}$  NMR. Further purification of this fraction with 1% ethyl acetate:hexane as an eluent gave **25** (93 mg, 59%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.92 (d, 2 H,  $J = 8.4$  Hz), 7.43 (d, 2 H,  $J = 8.2$  Hz), 4.88 (s, 2 H), 2.58 (s, 3 H), 1.80–1.28 (br m, 6 H), 1.22 (s, 6 H), 1.15 (s, 6 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  197.81, 143.95, 136.14, 128.43, 127.08, 78.19, 60.12, 39.75, 33.10, 26.67, 20.34, 17.14. MS (EI)  $m/z$  (rel intensity): 289 ( $\text{M}^+$ , 1), 156 (100). HRMS (EI)  $m/z$  ( $\text{M}^+$ ): calcd 289.2042, obsd 289.2067.

**Photoreduction of 9 by PhSH.** In conditions analogous to those for photoreaction of **8**, a solution of 0.02 M phosphonate **9**, 0.04 M PhSH, and 0.0031 M tri-*n*-butyl phosphate (internal standard) was irradiated. At 32% conversion of **9** (approximately 9 h), three major GC peaks were detected. One peak had a molecular ion mass (GC/MS) at  $m/z = 244$ , consistent with the product of reduction of the carbonyl of **9** to form *p*-MeCH(OH) $\text{C}_6\text{H}_4\text{CH}_2\text{P}(\text{O})(\text{OMe})_2$ . However, the latter product was not observed during the photorearrangements of phosphite **8**.

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**Supporting Information Available:** Experimental details for the preparation of **21**, products of dark reaction of **8** with PhSSPh to give **29a–29c**, and an expanded version of Table 5 that includes individual yields of **16**, **17a**, **17b**, **22**, **23a**, and **23b** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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