Photochemistry of Substituted Benzyldiphenylphosphine Oxides

Ningning Zhao and Douglas C. Neckers*,[1]

Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403

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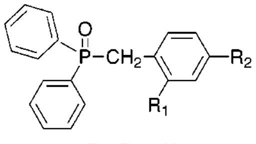
Photochemical reactions ($\lambda_{\rm irr} = 254$ nm) of substituted benzyldiphenylphosphine oxides **1a**−**e** have been investigated in benzene and acetonitrile. α-Cleavage from the singlet excited state is proposed as the primary process, and products formed both before and after escape of the primary intermediates from the solvent cage result. Radicals **2** and **3** are observed by nanosecond flash photolysis following excitation of **1a** at 266 nm in acetonitrile. Acetone sensitization of **1a**,**b** fails to improve the efficiency of product formation. The quantum yields of disappearance of **1a**,**b** are unaffected by O_2, and mechanisms for product formation from **1a** in the presence of oxygen are proposed.

Introduction

Acyl- and bis(acyl)phosphine oxides are efficient photoinitiators of radical polymerization.[2−7] Such compounds, the critical differentiating feature of which is formation of highly reactive phosphorus-centered radicals, are quite important commercially.[8−14] Time-resolved ESR experiments have shown that diphenylphosphinoyl radical has a large ^{31}P hyperfine coupling constant [(hfcc) ≈ 370 G[15]], indicating a high degree of σ character and significant spin localization on phosphorus. In some measure, this is proposed to account for its reactivity.

Benzyldiphenylphosphine oxides **1a**−**e** incorporate the phosphinoyl group but absorb shorter wavelength UV irradiation. Quantum yields for the disappearance of **1a**−**e** in both benzene and acetonitrile, and for the appearance of product **10**, in benzene are reported in this paper. We also examined the role of oxygen in the photoreaction of **1a**.



1a: R_1, R_2 = H
1b: R_1 = H, R_2 = CH_3
1c: R_1 = H, R_2 = OCH_3
1d: R_1 = CH_3, R_2 = H
1e: R_1 = OCH_3, R_2 = H

Results and Discussion

Photochemistry of 1a−e. Phosphine oxides **1a**−**e** were irradiated ($\lambda_{\rm irr} = 254$ nm) in acetonitrile or benzene. In a typical experiment, a 5×10^{-3} M degassed solution of **1a** in acetonitrile gave bibenzyl **10** as a major product, along with minor products **4**−**9** and trace amounts of 2-phenylpropionitrile, **15**, Scheme 1. Similar results were obtained for **1b**−**e**. Product yields as a function of irradiation time are shown in Table 1.

Product distributions suggest radical pairs **2** and **3** are generated from **1a** and undergo both solvent cage and diffusion processes, Scheme 1. Compound **10** is formed by radical recombination in significant yields (e.g., 80% at 15−94% conversion), while modest yields of products from cross-radical recombination (~10%) are also detected. Benzyldiphenyl phosphinite **4** and product **5**,[32b] intermediates isomers **6** and **8**, and the secondary products of tautormerization **7** and **9** account for about 10% of the benzyl radical generated.

Products resulting from the dimerization of **2**, tetraphenylphosphine dioxide **11**, and the product of its decomposition, diphenylphosphinic acid **22**, can be identified using ^{31}P NMR. Since **11** decomposes under the conditions of gas chromatography, its structure and those of its decomposition products were confirmed by comparison with authentic compounds. Hydrogen abstraction from solvent produces diphenylphosphine oxide and toluene. These are potentially formed in minor amounts in acetonitrile and not detected.

The products formed from irradiations of **1a** in benzene develop at different rates and in different distributions, Table 1. At 30% conversion, the yield of **4**−**9** (~20%) formed from the solvent cage process is obviously higher than is the yield formed from radicals escaping the

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* To whom correspondence should be addressed. Phone: (419) 372-2034. Fax: (419) 372−0366. E-mail: neckers@photo.bgsu.edu.

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Scheme 1. Photochemistry of 1a in Benzene and Acetonitrile in the Absence and Presence of Oxygen

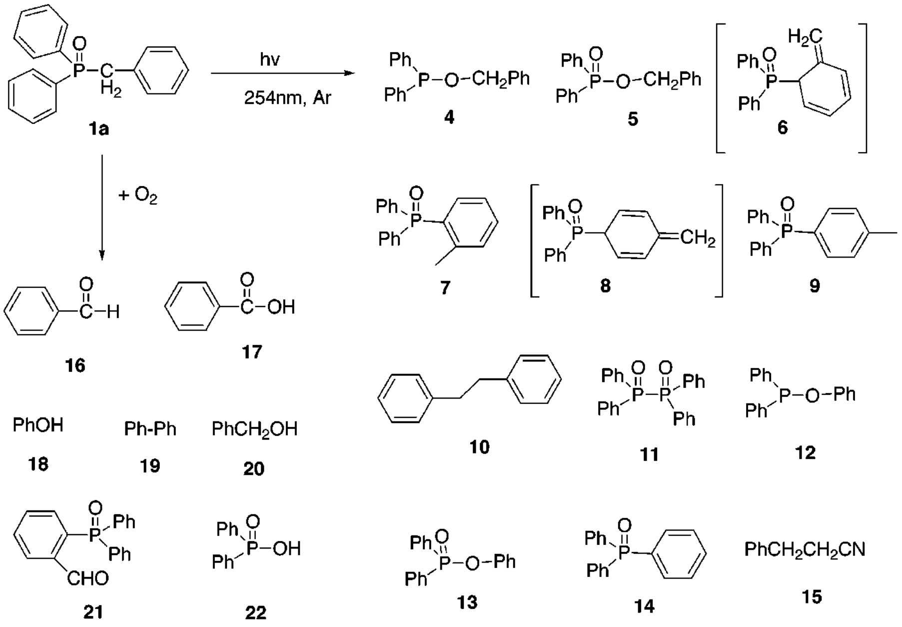

Table 1. Products of the Irradiation of 1a (5 × 10^{-3} M) in Acetonitrile/Benzene

	convn of **1**[c]	product accountability %[a]							
solvent	(%)	**4**	[**6**] + **5** + **7**	[**8**] + **9**	**10**[b]	**12**	**13**	**14**	**15**
CH_3CN	15		1.3	0.19	13.4				
	36		8.5	2.6	24.6				
	81		6.2		74			trace	
	95		8.7		82.5				trace
benzene	15	0.12	4.2	8.3	1.7				
	30	0.52	5.5	15	7.6			0.20	
	45	1.2	8.0	20.4	13			1.3	
	73	1.3	7.4	14.6	47			2.3	
	83	1.9	10.6	13.6	52			4.4	
	98	1.2	8.9	4.4	74	trace	trace	5.8	

[a] Based on the consumed **1**. The GC factors are predetermined, using decane as internal standard. Product **11** is not included. [b] Yield of **10** doubled account for the stoichiometry of its formation from 1. [c] Total irradiation time is 2 h.

solvent cage (~7%). At higher conversions, **10** and **11**, both products of cage escape, remain major though trace amounts of photoproducts **12**−**14** are also formed. These likely come from the addition of the phosphinoyl radical **2** to benzene forming the cyclohexadienyl adduct,[16] Scheme 2.

The ^{31}P NMR spectrum of the photolysis mixture formed from **1a** in benzene clearly shows resonances of all the major photoproducts that contain phosphorus **7**, **8**, **9**, and **11**, though the resonance at 29.378 ppm, corresponding to isomer **8**, overlaps with that at 29.113 ppm corresponding to isomer **9**. The individual isomers **7** and **9** have been identified by co-injection of authentic compounds on GC/MS. Since both **1a** and most of the photoproducts absorb at 254 nm, secondary reactions from primary photoproducts likely occur, and minor amounts of several secondary products are formed.

Photochemistry of 1a−e with O$_2$ Present. Irradiation ($\lambda_{\text{irr}} = 254$ nm) of 5×10^{-3} M solution of **1a** in an O$_2$-saturated solution in acetonitrile yields benzaldehyde **16**, benzoic acid **17**, and 2-(diphenylphosphinoyl)benzaldehyde **21**.

Solvent cage recombination products are formed in approximately the same amounts in the presence of O$_2$, though **4** undergoes further oxidation to form **5**, Table 2. Oxygen dramatically affects the yield of bibenzyl with **16**, **17**, and **21** being formed instead. Similarly, product **11** resulting from phosphinoyl radical coupling is not observed. Instead, diphenylphosphinic acid **22** with a known ^{31}P NMR resonance at 34.07 ppm can be detected.

Irradiation of **1a** in benzene leads to products and distributions differing from those obtained in acetonitrile. The yield of benzaldehyde, **16** (~34%), decreases from ~84% in acetonitrile while that of **21** increases from <1% to ~15%. Secondary products **17**, **18**, and **21** are formed in significant amounts while benzoic acid is formed in trace amounts during the entire irradiation. Photoproducts **12**−**14** are formed in benzene but not in acetonitrile. In the presence of O$_2$, **12** disappears and **13** is obtained instead.

Mechanism. Proposed mechanisms that account for all photoproducts are shown in Schemes 3 and 4, respectively. α-Cleavage of the benzyl carbon/phosphorus bond produces the phosphinoyl radical **2**, which is known to have two spin density distributions,[17] and the benzyl radical **3**, which can be thought of as a hybrid of several resonance contributors. As a result, multiple products from geminate radical recombination between phos-

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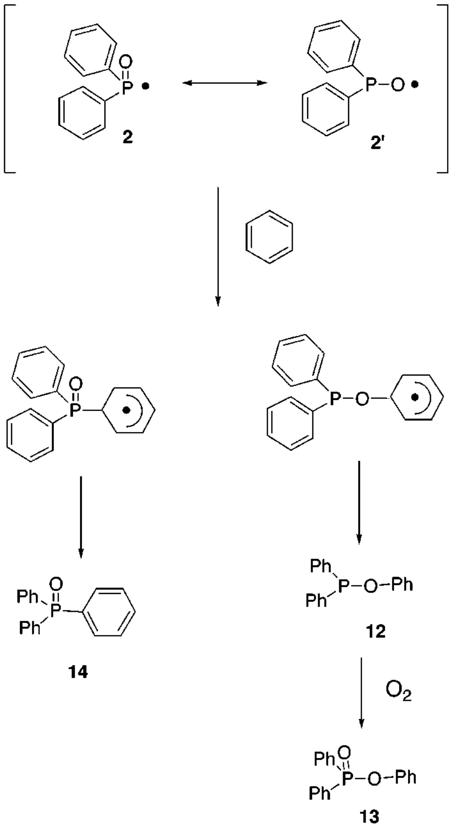
Table 2. Products of the Irradiation of 1a (5×10^{-3} M) with O_2 Present in Acetonitrile/Benzene

solvent	convn of **1**[b] (%)	product accountability[a] (%)									
		[**6**] + **5** + **7**	[**8**] + **9**	**13**	**14**	**16**	**17**	**18**	**19**	**20**	**21**
CH_3CN	8	1.9	2.0		2.5	trace					0.2
	15	4.0	3.4		2.0	16	trace				0.6
	52	12.5	trace		11.0	19	9.0				
	87	12.3			14.4	50	10.5				
	98	3.8			5.3	83.6	5.2				
benzene	15	3.6	4.3	2.2							4.5
	30	7.4	8.8	1.7		trace		trace	trace		13
	60	9.1	10.8	1.2	1.0	13.3		4.9	2.4		15.4
	81	10.7	8.7		1.2	22.8		15.6	5.6		15.5
	90	10.6	6.1		2.7	28.2		20.7	7.6		14.1
	95	8.7	4.5		4.2	33.6	trace	23	10	trace	12.6

[a] Based on the consumed **1**. The GC factors are predetermined, using decane as internal standard. Product **22** is not included. [b] Total irradiation time is 2 h.

Scheme 2. Mechanism of Benzene Scavenging of Phosphinoyl Radical 2



phinoyl radicals **2**, **2′** and the benzyl radical can occur. **4**, which results from recombination of **2′** and **3**, may be further oxidized to **5**. **6** and **8** result from the recombination of **2** and **3′**, **3″** respectively. Subsequent 1,3 and 1,5 H-atom shifts of **6** and **8** to more stable products **7** and **9**, respectively, are expected to be facile photochemical processes. An attempt to isolate these products by column chromotography was not successful, so comparison samples of **4**, **7**, and **9** were synthesized. Cross-radical recombination products **5**−**9** would not have formed in the presence of O_2, were there no solvent-cage processes occurring.

In acetonitrile, hydrogen abstractions between either radical **2** or **3** and the solvent may occur. Toluene likely elutes with solvent and was not detected. As for phosphinoyl radical **2**, the rate constant of hydrogen abstraction with benzhydrol (Ph_2CHOH) in hexane has been calculated to be less than 5×10^5 M^{-1} s^{-1}.[9] Since the bond strength of the H-atom donor dictates the rate constant of hydrogen abstraction, Ph_2CHOH (87 kcal/mol) < CH_3CN (93 kcal/mol),[18] the rate constant of hydrogen abstraction from acetonitrile must be much lower than 5×10^5 M^{-1} s^{-1}. When compared to the coupling rate constant of phosphinoyl radical $\sim 1.3 \times 10^{10}$ M^{-1} s^{-1},[19] formation of diphenylphosphine oxide is not a favorable process.

It is well-established that the rate constant for reaction of the benzyl radical with O_2 is in the range of 3.0×10^9 M^{-1} s^{-1}.[20] Since this is at least 1 order of magnitude faster than the recombination rate constant of two benzyl radicals $(3-20) \times 10^8$ M^{-1} s^{-1},[21,27b] benzylperoxy radical formation is more favorable than benzyl radical coupling.

In addition, the rate constant for reaction of the phosphinoyl radical with O_2 (5.3×10^8 M^{-1} s^{-1})[12,19] is slower than that of phosphinoyl radical recombination (1.3×10^{10} M^{-1} s^{-1}.)[19] Since reaction of **1a** is carried out with atmospheric O_2, moisture may also be inadvertently introduced during irradiation. Some hydrolysis of **11** may occur forming diphenylphosphinic acid **22**.

Solvent affects the formation and distribution of photooxidized products, Table 2. The proposed reaction of benzyl radical with O_2 leading to formation of benzylperoxy radical results in a situation where cross-radical recombination and inter- and intramolecular hydrogen abstraction processes compete, Scheme 4. Though acetonitrile is a poor hydrogen donor, intermolecular hydrogen abstraction processes may occur, and the resulting benzyl peroxide subsequently is converted to benzaldehyde **16**. Self-coupling of peroxy radicals may result in benzaldehyde and phenylmethyl alcohol.[22] Benzoic acid **17** is a secondary product resulting from oxidation of benzaldehyde.[23]

In non-hydrogen-donating solvents such as benzene, intramolecular hydrogen abstraction processes may occur. The putatively formed four-center intermediate is followed by the formation of benzylperoxide radical, Scheme 3. Such internal hydrogen abstraction is very likely for a resonance-weakened C−H bond such as allylic and benzylic −H. Energetically, the overall reaction has

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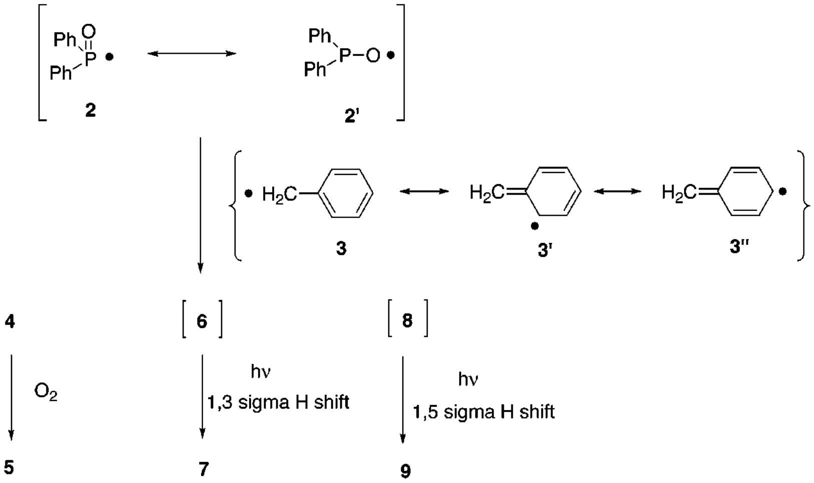
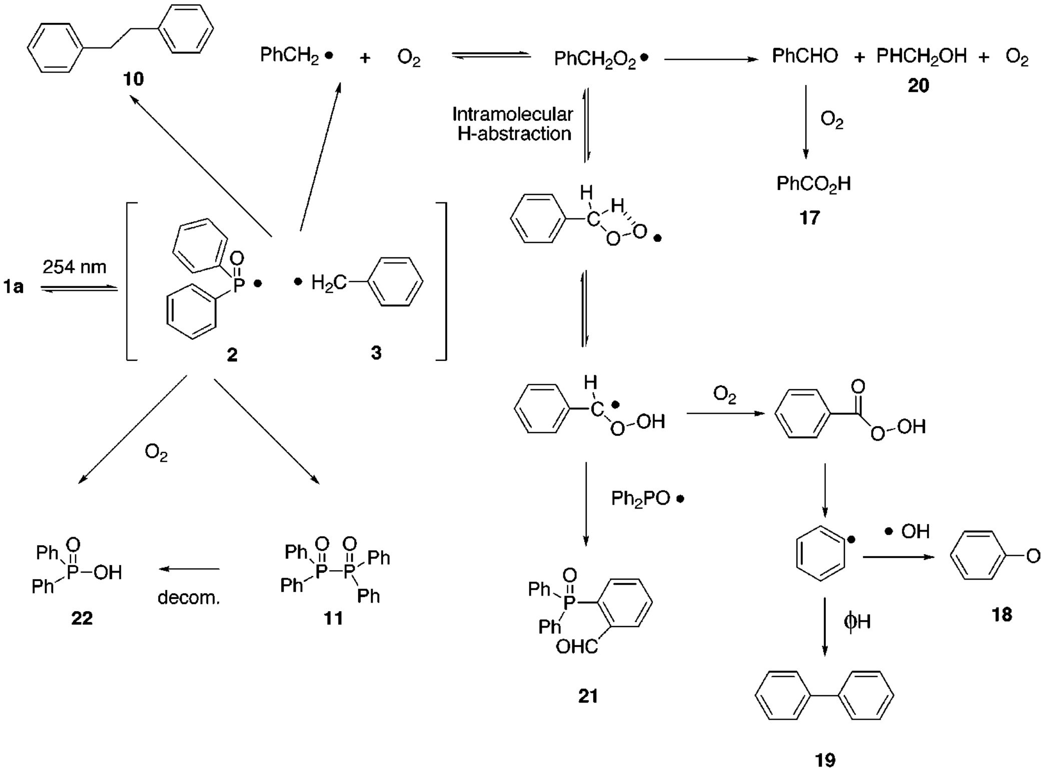
Scheme 3. Mechanism for the Process in the Solvent Cage



Scheme 4. Mechanism in Benzene and Acetonitrile in the Absence and Presence of Oxygen for Formation of Products outside the Solvent Cage



been calculated to be exothermic by 51−57 kcal/mol in gas phase.[24] The subsequent secondary reactions of the benzylperoxy radicals lead to formation of **18**, **19**,[25] and **21**.

Quantum Yields and the Nature of the Excited States. The quantum yields of disappearance of the phosphine oxides **1a**−**e** and of the appearance of bibenzyl **10** are reported in Table 3. **1a** turns out to be relatively more reactive than the *p*- and *o*-methoxybenzyldiphenylphosphine oxides **1c** and **1e**.

Quenching of the photoreactions of either **1a** or **b** with O_2 results in no decrease in the quantum efficiency of disappearance, though reaction with O_2 accounts for the formation of products **16**, **17**, **20**, and **21** and subsequent secondary products. There are other literature examples where oxygen apparently has no affect on the photoefficiency of reaction of benzylic compounds.[26]

Sensitization studies of **1a**−**e** are difficult because there are few sensitizers with triplet energies high enough to enable energy transfer. Attempted sensitization of the reactions of **1a**,**b** using acetone (E_T ~78 kcal/mol) leads to substantially lower efficiencies. A sufficiently high acetone concentration (OD > 2 at 313 nm) in benzene ensures minimal competitive absorption of **1a**,**b**. Since the photoproducts form but at much lower

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Table 3. Quantum Yields of Disappearance of Substituted Benzyldiphenylphosphine Oxides 1a–e in Benzene

	1a	**1b**	**1c**	**1d**	**1e**
ϕ_{dis}[a]	0.3 ± 0.03	0.29 ± 0.04	0.06 ± 0.05	0.27 ± 0.04	0.07 ± 0.008
ϕ_{app}(**10**)[a]	0.0005				
$\phi_{dis}(O_2)$[a]	0.27 ± 0.04	0.2 ± 0.03			
ϕ_{dis}(acetone)[b]	0.0001	0.0007			

[a] Quantum yields are measured within 5% conversion at 254 nm irradiation (actinometer: cyclohepta-1,3-diene $\phi = 4.6 \pm 0.01$ at 10^{-2} M in ethanol);[37] decane is used as an internal standard; ϕ_{dis} is the disappearance of **1a**–**e**; ϕ_{app}(**10**) is the appearance of bibenzyl; $\phi_{dis}(O_2)$disappearance of **1a**,**b** with O_2 saturated solutions. [b] ϕ_{dis}(acetone) is the disappearance of **1a**,**b** with addition of acetone (OD > 2 at 313 nm) using 2-hexanone as an actinometer ($\phi_d = 0.327$ at 1 M in pentane).[38]

efficiencies (Table 3), this result suggests a less reactive triplet excited state.

Nanosecond Laser Flash Photolysis. Laser flash photolysis of **1a**–**e** using 266 nm excitation gives similar transient absorption spectra in acetonitrile and cyclohexane. The transient absorption between 280 and 400 nm has been assigned to the overlap of the absorptions of the benzyl and phosphinoyl radicals. The decay of this transient, monitored at 320 nm, follows clean biexponential kinetics on the microsecond scale. The fast component is phosphinoyl radical with a lifetime of ~6 μs. The slow component is a long-lived species that does not decay completely over 1 ms; the longest time scale of our analyzing light and laser system. It is assigned to the benzyl radical that has a lifetime of ~139 μs. Similar transient absorptions and lifetimes of benzyl and phosphinoyl radicals have been reported.[8,12,19,27]

The lifetimes of the radicals change with concentration of **1a**–**e**. In addition, triplet absorption is not detected on the nanosecond scale. As a result, it is very likely that radicals are generated from the singlet excited state.

Conclusion. The photoreactions of phosphine oxides **1a**–**e** proceed primarily via singlet excited states with the resulting photoproducts deriving from both solvent cage and cage escape processes. The presence of oxygen does not seriously affect the reaction efficiency though some oxidized products are obtained.

A complete mechanism for the photoreaction of benzyl diphenylphosphine oxide based on extensive studies of various phosphine oxides has been proposed. Further exploitation of benzyldiphenylphosphine oxide photochemistry both in photoinitiation and protecting group applications is vigorously underway in this laboratory.

Experimental Part

Materials and Solvents. Benzene (Aldrich) was dried over sodium under Argon. Chlorodiphenylphosphine was obtained from Lancaster. Unless mentioned, all other chemicals and solvents (anhydrous grade) were obtained from Aldrich and used as received.

General Methods. Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. NMR spectra were obtained either with a Varian Gemini 200 NMR spectrometer or Varian Unity Plus 400 NMR spectrometer. Chemical shifts are in ppm with TMS as the internal standard (^{1}H NMR and ^{13}C NMR) or H_3PO_4 as the external standard (^{31}P NMR). GC/MS and MS spectra were obtained on a Shimadzu GC/MS-QP5050 mass spectrometer coupled to a GC-17A (Restek ST1-5 column 30 m × 0.25 mm × 0.25 μm). Quantitative GC analysis utilized decane as an internal standard against which all other peaks were calibrated for sensitivity (response factor), except as mentioned otherwise. Infrared spectra were taken with a Galaxy series 6020 FTIR spectrometer. Thin-layer chromotography was performed with Whatman silica gel coated TLC plates. Absorption spectra were recorded using a Hewlett-Packard 8452A diode array UV–vis spectrophotometer.

Benzyldiphenylphosphine Oxide (1a).[28] Diphenylmethyl phosphinite (0.005 mol) was added dropwise to benzyl chloride (0.005 mol). The reaction mixture was then heated to 100 °C and stirred at that temperature for 30 min. After the solution was cooled, a white solid appeared. The crude product was purified by crystallization from ethanol affording 1.4 g (97% yield) of **1a**: white needles; mp 189–190 °C (lit.[29] mp 192–193 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.689–3.619 (d, J = 14 Hz, 2 H), 7.101–7.2 (m, 5 H), 7.393–7.517 (m, 6 H), 7.642–7.746 (m, 4 H); ^{13}C NMR (50 Hz, $CDCl_3$) δ 38.750–37.421 (d, J = 66.45 Hz), 126.769–126.697 (d, J = 3.6 Hz), 128.334, 128.553, 130.045–130.154 (d, J = 5.45 Hz), 131.046–131.226 (d, J = 9.1 Hz), 131.282, 131.710–131.774 (d, J = 2.75 Hz), 133.248–134.430 (d, J = 59.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.430; MS m/e 292 (16.2, M^+), 291 (30.4), 202 (14.2), 201 (100), 183 (4.2), 152 (4.7), 91 (10.6), 77 (29.6).

***p*-Methylbenzyl iphenylphosphine Oxide (1b).**[28] A procedure similar to that described for **1a** produced **1b** in 87% yield: white needles; mp 198–199 °C (lit.[30] 196 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.251 (s, 3 H), 3.583–3.651 (d, J = 13.6 Hz, 2 H), 6.988 (s, 4 H), 7.422–7.7 (m, 10 H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.412; MS m/e 306 (18.6, M^+), 305 (36.6), 202 (13.8), 201 (100), 183 (4.5), 181 (6.7), 123 (2), 105 (17.5), 77 (46).

***p*-Methoxybenzyldiphenylphosphine oxide (1c).**[28] A procedure similar to that described for **1a** produced **1c** in 92% yield: white needles; mp 227–228 °C (lit.[31] 228–229 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.564–3.632 (d, J = 13.6 Hz, 2 H), 3.748 (s, 3 H), 6.709–6.752 (q, J = 8.6 Hz, J = 2.2 Hz, 2 H), 6.992–7.036 (q, J = 8.8 Hz, J = 2.2 Hz, 2 H), 7.429–7.737 (m, 10 H); ^{31}P NMR (162 MHz, C_6D_6) δ 29.298; MS m/e 322 (10.5, M^+), 321 (9.7), 202 (3.5), 201 (25.6), 197 (6.5), 152 (2.2), 121 (100), 122 (8.9), 77 (26.5).

***o*-Methylbenzyldiphenylphosphine Oxide (1d).**[28] A procedure similar to that described for **1a** produced **1d** in 59% yield: white needles; mp 122–123 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.113 (s, 3 H), 3.667–3.702 (d, J = 14 Hz, 2 H), 6.9 (m, 2 H), 7.0 (m, 2 H), 7.4–7.7 (m, 10 H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.803; MS m/e, 306 (42.5, M^+), 291 (3.6), 215 (3.8), 201 (100), 183 (5.3), 181 (8.1), 165 (4.7), 152 (3.8), 105 (9.1), 91 (1.8), 77 (45.3); HRMS m/e measured 306.1171, calcd 306.1167.

***o*-Methoxybenzyldiphenylphosphine Oxide (1e).**[28] A procedure similar to that described for **1a** produced **1e** in 71% yield: white solid; mp 107–108 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.450(s, 3 H), 3.735–3.771 (d, J = 13.6 Hz, 2 H), 6.649–6.670 (d, J = 8.4 Hz, 1 H), 6.850–6.887 (t, J = 7.6 Hz, 7.2 Hz, 1 H), 7.123–7.163 (t, J = 7.2 Hz, 1 H), 7.356–7.727 (m, 11 H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.052; MS m/e 322 (35.8, M^+), 304 (19.1), 291 (6.4), 201 (100), 183 (6.4), 165 (4), 152 (5.2), 121 (25.3), 91 (57.8), 77 (37.9); HRMS m/e measured 322.1228, calcd 322.1227.

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Benzyldiphenyl phosphinite (4):[32] crude yield 83%; bp 220−30 °C,[32a] characterized without purification; ^{31}P NMR (162 MHz, C_6D_6) δ 118.1; MS *m/e* 292 (5, M$^+$), 291 (15.2), 201 (100), 183 (6.5), 152 (3.7), 107 (3.1), 91 (17.3), 77 (26.7).

***o*-Methylphenyldiphenylphosphine oxide (7):**[33] 86% yield; white solid; mp 120−121 °C (lit.[33] mp 122−123 °C); ^{1}H NMR (200 MHz, C_6D_6) δ 2.581 (s, 3 H), 7.0−7.3 (m, 3 H), 7.4−7.7 (m, 11 H); ^{31}P NMR (162 MHz, C_6D_6) δ 32.149; MS *m/e* 292 (49, M$^+$), 291 (100), 213 (16), 199 (7.5), 183 (6), 166 (14.4), 165 (27.4), 152 (8.4), 91 (5.5), 77 (11.8).

***p*-Methylphenyldiphenylphosphine oxide (9):**[34] 95% yield; white solid; mp 129−130 °C (lit.[34] mp 129−130 °C); ^{1}H NMR (200 MHz, C_6D_6) δ 1.957 (s, 3 H), 6.827−6.880 (q, J = 8.4 Hz, J = 2.2 Hz, 2 H), 6.992−7.052 (m, 6 H), 7.651−7.851 (m, 6 H); ^{31}P NMR (162 MHz, C_6D_6) δ 29.094; MS *m/e* 292 (50.8, M$^+$), 291 (100), 215 (15.6), 213 (14), 201 (4.3), 199 (20), 183 (11.9), 165 (8.7), 152 (9.8), 91 (11.2), 77 (21).

Tetraphenylphosphine dioxide (11):[35] mp 167−168 °C (lit.[35] mp 168−169 °C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.8; MS *m/e* 402 (0.07, M$^+$), 277 (3.7), 217 (17.8), 202 (58), 201 (100), 183 (16.6), 152 (9.8), 124 (14.5), 77 (68.4).

2-(Diphenylphosphinoyl)benzaldehyde (21):[36] 95% yield; mp 146−7 °C (lit.[36] mp 120−121 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.487−7.683 (m, 14 H), 10.733 (s, 1 H); ^{31}P NMR (162 MHz, $CDCl_3$); δ 32.141; MS *m/e* 306 (34.4, M$^+$), 278 (23), 277 (100), 199 (53.4), 183 (12.1), 152 (30), 77 (29.4); IR (cm^{-1}) 2940 (CHO), 1689 (C=O), 1189 (P=O).

Photolysis of 1a−e. The benzyldiphenylphosphine oxides were dissolved in benzene or acetonitrile in a quartz cuvette and sealed with a rubber septum bound by sticky Parafilm, and the solution was degassed by bubbling with dry argon gas for 10−15 min. The solution was irradiated for 3−120 min in a Rayonet RPR 100 photoreactor, equipped with 16 254 nm F8T5-BLB UV lamps. The products were identified by comparison with authentic samples, which were synthesized or purchased.

Quantum Yield Measurements. Light intensity was determined using the reaction of cyclohepta-1,3-diene in ethanol ($\phi = 0.46 \pm 0.01$ at 0.01 M) at 254 nm.[37] The progress of the reaction was monitored by GC/MS analysis. Decane was used as an internal standard in GC calibration and for quantitative measurements. The values reported in Table 3 are the average of three experiments.

Acetone-Sensitized Photolysis of 1a,b in Benzene. Each sample solution in benzene with high acetone concentration (OD > 2 at 313 nm) was irradiated with 200W mercury lamp at 313 nm using 313 ± 10 nm band glass filter. 2-Hexanone in pentane solution (1 mol/L, $\phi_d = 0.327$, $\lambda_{ex} = 313$ nm)[38] was used as an actinometer. Decane was used as an internal standard in GC calibration and quantitative measurements.

Laser Flash Photolysis. Nanosecond laser flash photolysis experiments were carried out on a setup described by Ford and Rodgers using a Q-switched Nd:YAG laser as a pump light (355 nm; 60 mJ/pulse; 8 ns pulse or 266 nm; 5 mJ/pulse; 8 ns pulse).[39] Argon, oxygen, or air was bubbled continuously through the sample solution during the measurements.

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