

(2,4,6-Trimethylbenzoyl)diphenylphosphine Oxide Photochemistry. A Direct Time-Resolved Spectroscopic Study of Both Radical Fragments

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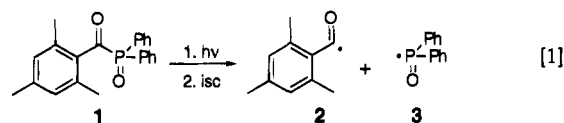
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Abstract: The photochemistry of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (**1**) has been investigated using time-resolved infrared (TRIR) and time-resolved UV spectroscopy (laser flash photolysis (LFP)), in addition to conventional photochemical steady-state techniques and product analysis. Direct photolysis of **1** in dichloromethane (CH₂Cl₂) or *n*-heptane solution causes α -cleavage to afford the corresponding 2,4,6-trimethylbenzoyl (**2**) and diphenylphosphonyl (**3**) radicals. The 2,4,6-trimethylbenzoyl radical (**2**) is readily detected using TRIR spectroscopy, exhibiting carbonyl IR absorption maxima at 1805 and 1797 cm⁻¹ in *n*-heptane and CH₂Cl₂ solution, respectively. The diphenylphosphonyl radical (**3**) is readily detected by LFP, exhibiting a strong UV absorption in the 300–350 nm region. Rate constants for the reactions of radicals **2** and **3** with bromotrichloromethane (BrCCl₃), thiophenol (PhSH), and benzhydrol (Ph₂CHOH) have been determined. Both radicals react with BrCCl₃ and PhSH via atom abstraction with rate constants in the 10⁷–10⁸ M⁻¹ s⁻¹ range. Photolysis of **1** in the absence of a radical scavenger affords diphenyl[(2,4,6-trimethylbenzoyl)oxy]phosphine (**9**) in addition to the expected free radical-derived products. Compound **9** is also produced upon photolysis of **1** in the presence of 0.05 M BrCCl₃, indicating that it is formed mainly via cage recombination of radicals **2** and **3**. The reactivity of radicals **2** and **3** is discussed.

Introduction

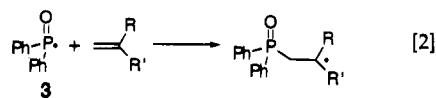
Benzoylphosphine oxides are an important class of polymerization photoinitiators.^{1–3} Photolysis of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (**1**) affords 2,4,6-trimethylbenzoyl (**2**) and diphenylphosphonyl (**3**) radicals (see eq 1) via α -cleav-



age from a short-lived ($\tau < 1$ ns) triplet excited state.^{1–3} The high efficiency of the reaction ($\phi \approx 0.6$),¹ coupled with the strong absorption of **1** in the near UV and its stability toward hydrolysis, has led to its development as a commercial photoinitiator for curing of polymer resins.³ Phosphonyl radical **3** is 1–2 orders of magnitude more reactive than the benzoyl radical **2** toward unsaturated substrates.^{1,2,4,5} Thus, numerous studies of the addition of the diphenylphosphonyl radical (**3**) to a variety of unsaturated compounds such as alkenes,^{1,2,4} dienes,⁵ nitrones,⁶

thiocarbonyls,⁷ quinones,⁸ oximes,⁹ and pyridines¹⁰ have been reported. Conversely, the reactivity of **2** has been incompletely documented.

Laser flash photolysis (LFP) techniques have been employed to detect **3** directly in solution ($\lambda_{\text{max}} = 330$ nm) and to determine absolute bimolecular rate constants for its addition to a series of alkenes ($k \approx 10^6$ to 6×10^7 M⁻¹ s⁻¹).^{1,2} Rate constants for the reaction of **3** with alkenes and dienes have been measured using time-resolved electron spin resonance (TR-ESR) (see eq 2).^{4,5}



The 2,4,6-trimethylbenzoyl radical (**2**) has been detected directly by TR-ESR^{6,11,12} in solution at room temperature and by UV-vis absorption spectroscopy in an organic matrix at 77 K ($\lambda_{\text{max}} \approx 500$ nm).¹³ The UV absorption spectrum of **2** in solution has not been reported; however, it is expected to be similar to that of the unsubstituted benzoyl radical (**4**) which exhibits a weak transient absorption at 368 nm ($\epsilon \approx 150$ M⁻¹

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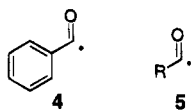
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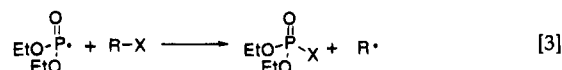
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cm^{-1}).¹⁴ Such a weak extinction carries with it a significant difficulty for characterization of benzoyl radicals in solution by time-resolved UV absorption spectroscopy. This difficulty has been recently overcome by the demonstration that time-resolved infrared (TRIR) spectroscopy is a powerful technique for direct detection of benzoyl and aliphatic acyl radicals.¹⁵ Rate constants for reaction of **4** with bromotrichloromethane,



carbon tetrachloride, and thiophenol were readily determined by this technique.¹⁵ TRIR spectroscopy has also been fruitfully applied in studies of other organic reactive intermediates such as ynols,¹⁶ ketenes,¹⁷ cumyloxy radicals,¹⁸ and dideoxazepines.¹⁹

Although the addition of the diphenylphosphonyl radical (**3**) to unsaturated compounds has been well documented, there have been no investigations, to our knowledge, of the reactions of **3** with hydrogen or halogen atom donors. Indeed, there is only a single report of the reaction of a related radical with a series of halocarbons (see eq 3).²⁰ The rates for halogen atom



abstraction by the diethoxyphosphonyl radical were found to be highly dependent upon the halocarbon ranging from $3.7 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ for *tert*-butyl chloride to $1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for benzyl bromide.²⁰

In this paper, we report the results of the study of the photochemistry of **1** by TRIR and LFP techniques. The 2,4,6-trimethylbenzoyl radical (**2**) has been directly characterized by TRIR, and rate constants for its reactions with bromotrichloromethane (BrCCl_3), thiophenol (PhSH), and benzhydrol (Ph_2CHOH) have been determined. The diphenylphosphonyl radical (**3**) has been directly characterized by LFP, and rate constants for its reactions with BrCCl_3 , PhSH , and Ph_2CHOH have been determined. Steady-state product studies have been carried out to supplement the time-resolved experiments.

Results and Discussion

Time-Resolved Infrared Spectroscopy. Laser flash photolysis (355 nm excitation) of 0.02 M solutions of **1** in deoxygenated *n*-heptane or dichloromethane (CH_2Cl_2) affords readily detectable transient IR absorptions in the 1780–1820 cm^{-1} region. These signals are formed within the response time of the TRIR detection system (<50 ns) and decay on the microsecond time scale with clean second-order kinetics ($\tau_{1/2} \approx 4\text{--}8 \mu\text{s}$). Figure 1 shows the time-resolved IR absorption spectrum in *n*-heptane recorded 1 μs following the laser pulse.

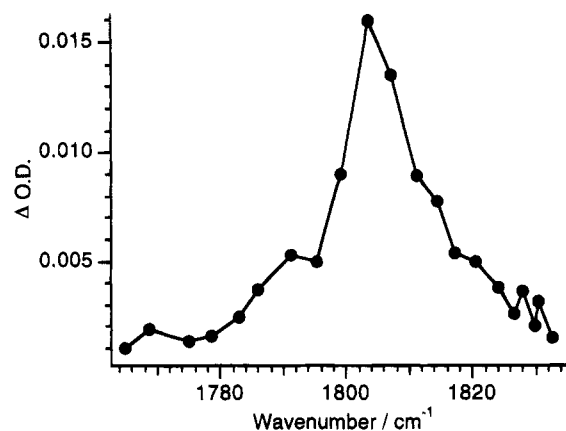


Figure 1. Time-resolved IR spectrum recorded 1 μs following laser flash photolysis (355 nm excitation) of a deoxygenated 0.02 M *n*-heptane solution of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (**1**) at $23 \pm 2 \text{ }^\circ\text{C}$.

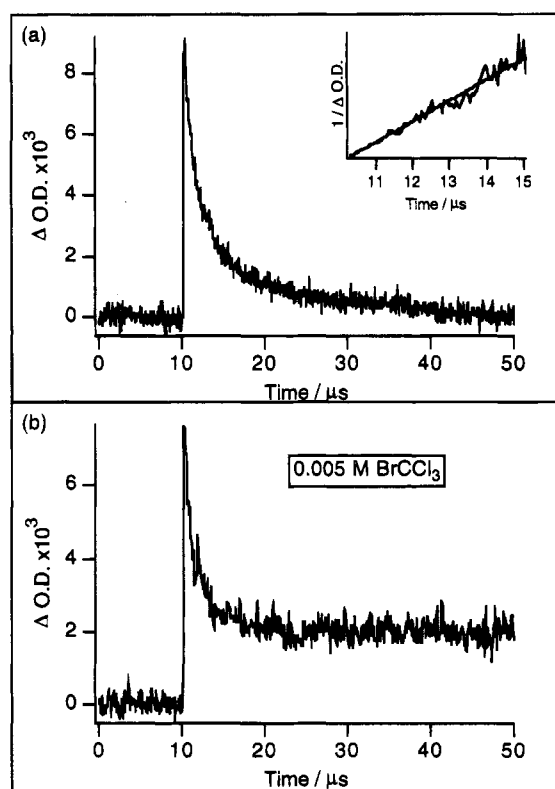


Figure 2. (a) Transient decay trace recorded at 1805 cm^{-1} from a 0.02 M solution of **1** in deoxygenated *n*-heptane. The inset shows the fit of the data according to eq 4. (b) Transient decay trace recorded at 1811 cm^{-1} from a 0.02 M solution of **1** in deoxygenated *n*-heptane containing 0.005 M bromotrichloromethane.

The spectrum is similar to those reported for the unsubstituted benzoyl radical (**4**) and a series of aliphatic acyl radicals **5**,¹⁵ all of which exhibit carbonyl IR absorption maxima in the range 1825–1860 cm^{-1} . The addition of BrCCl_3 , PhSH , or oxygen to solutions of **1** shortened the lifetime of the transient and lead to pseudo-first-order decay kinetics in each case. Representative decay traces recorded following laser flash photolysis of *n*-heptane solutions of **1** in the absence and presence of 0.005 M BrCCl_3 are shown in Figure 2. We assign the transient IR bands to the 2,4,6-trimethylbenzoyl radical (**2**) on the basis of its expected carbonyl stretching frequency,¹⁵ kinetic behavior and the identification of the reaction products (*vide infra*).

The IR absorption maximum of **2** exhibits a significant and reproducible shift from 1805 cm^{-1} in *n*-heptane to 1797 cm^{-1}

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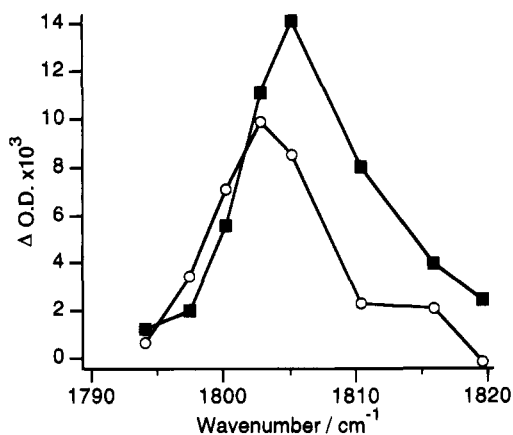


Figure 3. Time-resolved IR spectra, recorded (■) 1 μ s and (○) 40 μ s following the laser pulse, from laser flash photolysis (355 nm excitation) of a 0.02 M solution of **1** in deoxygenated *n*-heptane containing 0.005 M bromotrichloromethane.

in CH_2Cl_2 . The origin of the spectral shift is not obvious. However, the difference in the IR absorption maximum is not simply related to solvent polarity since preliminary experiments indicate that the absorption maximum is centered at 1800 cm^{-1} in a highly polar organic solvent such as acetonitrile. Furthermore, we note that the carbonyl IR absorption maximum of the acetyl radical **5** ($\text{R} = \text{CH}_3$) exhibits a strong matrix dependence.²¹

The kinetic data for the decay of **2** in the absence of added quencher were analyzed by plotting $(\Delta(\text{OD}))^{-1}$ versus time (t) according to eq 4. The pseudo-first-order rate constant, k_{obs} , is related to the second-order decay rate constant ($2k_2$) according to eq 5 where ϵ is the extinction coefficient of the carbonyl

$$(\Delta(\text{OD}))^{-1} = k_{\text{obs}}t \quad [4]$$

$$k_{\text{obs}} = 2k_2/\epsilon l \quad [5]$$

absorption and l is the IR cell path length (0.2 cm). The values of k_{obs} are 8.1×10^7 and $5.4 \times 10^7\text{ s}^{-1}$ in *n*-heptane and CH_2Cl_2 , respectively. We estimate the second-order decay rate constants ($2k_2$) to be near the diffusion-controlled limits for both solvents ($\sim 10^{10}\text{ M}^{-1}\text{ s}^{-1}$) on the basis of the assumption that **2** has an ϵ similar to that of the benzoyl radical **4** ($\sim 1300\text{ M}^{-1}\text{ cm}^{-1}$).¹⁵ The small but reproducible difference in k_{obs} in *n*-heptane and CH_2Cl_2 is assigned to a slight solvent dependence on the carbonyl IR absorption extinction coefficient since the two solvents have similar viscosities at room temperature.²²

The decay of **2** in *n*-heptane solutions containing BrCCl_3 is accompanied by the concurrent growth of a signal centered at 1802 cm^{-1} , which is assigned to the carbonyl stretching frequency of 2,4,6-trimethylbenzoyl bromide (**6**) (see eq 6).

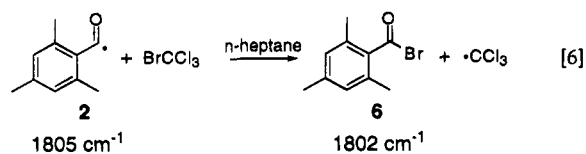


Figure 3 shows time-resolved IR spectra recorded 1 and 40 μ s following laser excitation (355 nm) of a 0.02 M solution of **1** in deoxygenated *n*-heptane containing 0.005 M BrCCl_3 . The spectrum recorded 1 μ s following the laser pulse is virtually

Table 1. Rate Constants for Reaction of 2,4,6-Trimethylbenzoyl (**2**) and Diphenylphosphonyl (**3**) Radicals with Bromotrichloromethane (BrCCl_3), Thiophenol (PhSH), and Benzhydryl (Ph_2CHOH) in Alkane Solution at $23 \pm 2\text{ }^\circ\text{C}$ ^a

reagent	k_q (10^{-8} Ms)	
	2	3
BrCCl_3	1.7	8.3
PhSH	0.13	0.15
Ph_2CHOH	$<0.005^b$	$<0.005^b$

^a Errors are ca. $\pm 10\%$. ^b Dichloromethane solution.

identical to that recorded in the absence of BrCCl_3 (see Figure 1) while the spectrum recorded at later times (40 μ s) is similar to the reported carbonyl spectrum of **6**.²³ The decay trace recorded at 1811 cm^{-1} under these conditions demonstrates the pseudo-first-order decay of **2** and residual absorption attributable to **6** (see Figure 2b).

Bimolecular rate constants for reaction of **2** with BrCCl_3 and PhSH were determined from the pseudo-first-order decay rates in the presence of sufficient quencher to shorten the lifetime to $\sim 1\text{ }\mu\text{s}$. Table 1 lists rate constants for reaction of **2** with BrCCl_3 , PhSH , and Ph_2CHOH . Radical **2** and the unsubstituted benzoyl radical (**4**) exhibit similar reactivities toward BrCCl_3 and PhSH , indicating that methyl substitution has only a small effect on the rates of atom abstraction reactions of benzoyl radicals.¹⁵ The rate constant for reaction of **2** with BrCCl_3 in *n*-heptane solution is only slightly smaller than the corresponding rate of reaction of **4**, while the rate constant for reaction of **2** with PhSH is a factor of 3 times smaller than that reported for **4**.¹⁵ Due to the low solubility of Ph_2CHOH in alkane solvents, the rate constant for reaction of **2** was determined in CH_2Cl_2 solution. The decay kinetics of **2** in CH_2Cl_2 were unaffected by the addition of 0.3 M Ph_2CHOH , permitting an estimate of the upper limit on the rate constant for hydrogen abstraction ($k < 5 \times 10^5\text{ M}^{-1}\text{ s}^{-1}$). The rates of reaction of **2** with BrCCl_3 in CH_2Cl_2 and *n*-heptane are identical within the experimental error. The lack of solvent dependence on the reaction rate indicates that bromine atom abstraction may occur via a nonpolar transition state. However, further experiments are required to elucidate the possible role of charge transfer processes in halogen atom abstractions of **2**.

Substitution on the phenyl ring of benzoyl radicals and benzoyl halides has a significant effect on their carbonyl IR maxima. The carbonyl IR absorption maximum of **2** in hydrocarbon solution (1805 cm^{-1}) is red-shifted over 20 cm^{-1} compared to that of the unsubstituted benzoyl radical (**4**) (1828 cm^{-1}).¹⁵ Conversely, the IR band of **6** (1802 cm^{-1}) is blue-shifted by ca. 20 cm^{-1} relative to that of benzoyl bromide (1780 cm^{-1}).¹⁵

Time-Resolved UV Spectroscopy. Laser flash photolysis (355 nm excitation) of continuously flowing 0.001 M deoxygenated hexane or CH_2Cl_2 solutions of **1** affords a readily detectable transient absorption in the 300–350 nm region (see Figure 4) which is assigned to the diphenylphosphonyl radical (**3**).¹ Although photoinduced intramolecular H atom abstraction leading to transient 1,4-biradicals and enols has been documented for several benzoylphosphine oxides,^{2,24} we have not obtained evidence for similar reactions of **1**.²⁴ In the absence of added quenchers, **3** decays on the microsecond time scale with mixed first- and second-order kinetics ($\tau_{1/2} \approx 10\text{ }\mu\text{s}$). The addition of BrCCl_3 , PhSH , or oxygen shortens the lifetime of **3** and leads to clean pseudo-first-order decay in each case.

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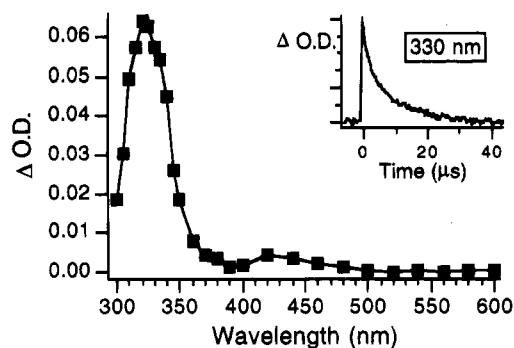


Figure 4. Transient UV absorption spectrum recorded 0.1–1.0 μs following laser flash photolysis (355 nm excitation) of a 0.001 M solution of **1** in deoxygenated hexane. The inset shows a transient decay measured at a monitoring wavelength of 330 nm.

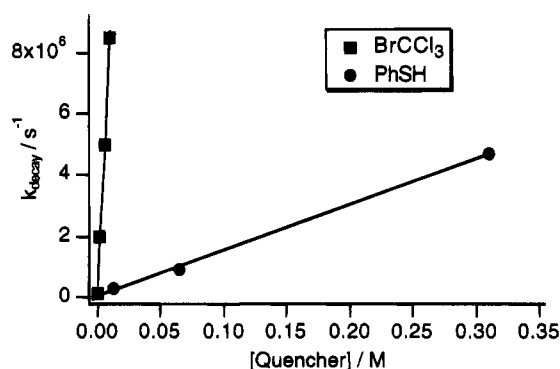
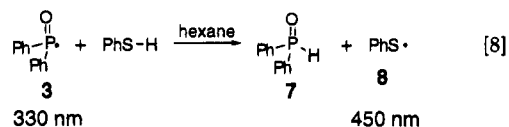


Figure 5. Pseudo-first-order decay rate (k_{decay}) of radical **3** versus quencher concentration for reaction with (■) bromotrichloromethane and (●) thiophenol.

Bimolecular rate constants (k_q) for reaction of **3** with BrCCl_3 and PhSH were obtained from plots of the pseudo-first-order rate constants for decay of **3** (k_{decay}) versus concentration of added quencher (see Figure 5) according to eq 7 and are listed

$$k_{\text{decay}} = k_0 + k_q[\text{Q}] \quad [7]$$

in Table 1. The term k_0 represents the estimated first-order rate constant for decay of **3** in the absence of added quencher. The lifetime of **3** in CH_2Cl_2 was unaffected by the addition of 0.1 M Ph_2CHOH , allowing us to estimate an upper limit of $5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for the quenching rate constant in this case. In the presence of PhSH , the decay of the diphenylphosphonyl radical (**3**) at 330 nm is accompanied by the growth of a transient absorption centered at 450 nm, which is assigned to the thiophenoxy radical (**8**; see eq 8).²⁵



The two radicals **2** and **3** generated from photolysis of **1** exhibit similar reactivities toward the atom donors employed in this study. The qualitative trend is for the rate constants to increase as the strength of the bond broken in the atom donors decreases: BrCCl_3 (56 kcal/mol)²⁶ > PhSH (75 kcal/mol)²⁷ > Ph_2CHOH (87 kcal/mol).²⁸ In each case, the rate constants for reaction of **2** and **3** with a particular atom donor are within a

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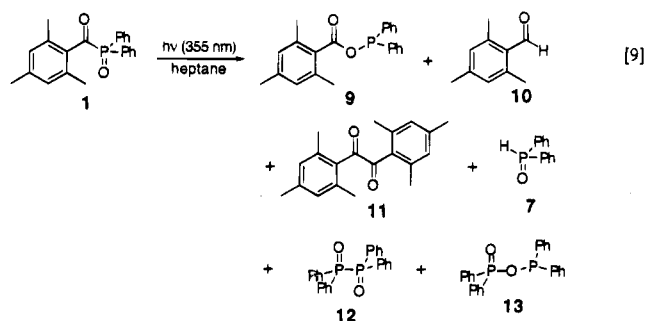
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factor of 4 (see Table 1). The phosphorus-centered radical **3** shows a slight rate enhancement toward BrCCl_3 while **2** and **3** react at almost the same rate with PhSH . The high reactivity of **2** and **3** toward atom donors is attributable to the fact that they are σ radicals with a high degree of s-character and spin density localized on the carbonyl carbon and phosphorus atoms, respectively.^{14,29} The similar reactivity of **2** and **3** toward atom abstraction in this case is notable, since the phosphonyl radical reacts with unsaturated compounds 10–100 times faster than the benzoyl radical.^{1,2,4,5} This implies that the transition states for additions of **2** and **3** to unsaturated compounds may be situated slightly further along the reaction coordinate than the transition states for atom abstraction reactions, and steric and electronic effects may play a larger role.³⁰

Product Studies. Steady-state product studies have been conducted to identify the products of reactions of radicals **2** and **3** with BrCCl_3 and PhSH . Photolysis (355 nm excitation) of a deoxygenated 0.005 M solution of **1** in *n*-heptane (or hexane) in the absence of an added radical trapping agent afforded the products shown in eq 9. Similar product distribu-



tions were obtained from photolysis of **1** in deoxygenated and dried CH_2Cl_2 .³¹ Diphenyl[(2,4,6-trimethylbenzoyl)oxy]phosphine (**9**), 2,4,6-trimethylbenzaldehyde (**10**), and mesitol (**11**) were the sole carbonyl-containing products identified, while the identified other products consisted of diphenylphosphine oxide (**7**) and two isomeric diphosphorus compounds (**12**, **13**). Compounds **7**, **9**, and **10** were identified by comparison of the IR, NMR, and GC/MS analyses of the crude photolysates with authentic samples.^{32,33} Mesitol (**11**) was identified by steady-state IR and GC/MS analysis of the crude photolysates. Compounds **12** and **13** have been tentatively assigned by ³¹P NMR spectroscopy³³ as they presumably decompose under our GC conditions.

All of the products from photolysis of **1** in the absence of a radical trap are those expected from reactions of radicals **2** and **3**. Similar product distributions were obtained from photolysis of benzene solutions of **1** in the presence of 1,1-di-*p*-tolylethylene due to incomplete trapping of **2** and **3**.³⁴ 2,4,6-Trimethylbenzaldehyde (**10**) and diphenylphosphine oxide (**7**) are most

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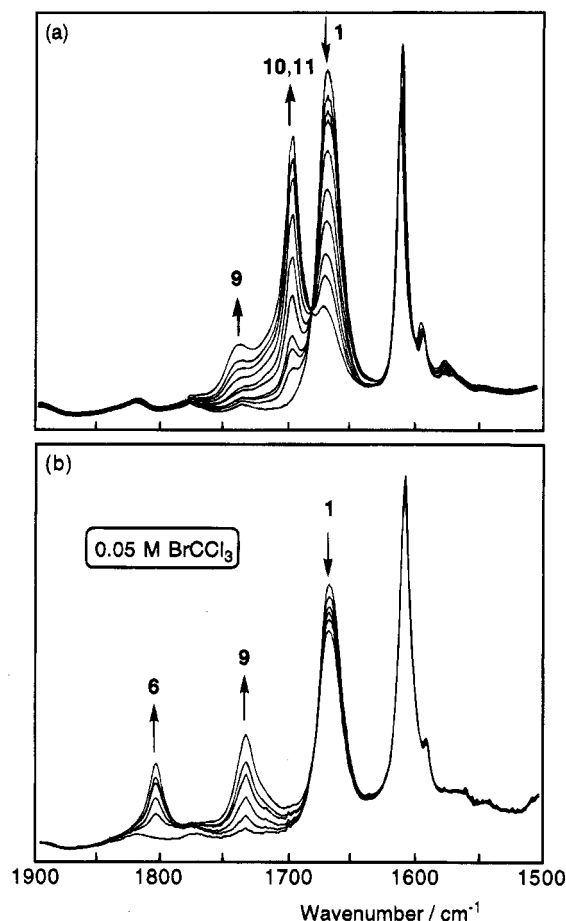
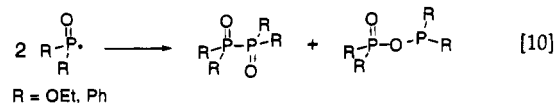


Figure 6. Steady-state FTIR spectra recorded from photolysis (355 nm excitation) of deoxygenated 0.005 M dichloromethane solutions of **1** (a) in the absence and (b) in the presence of 0.05 M bromotrichloromethane.

likely formed by hydrogen atom abstraction from solvent by **2** and **3**, respectively. Mesityl (**11**) arises from dimerization of benzoyl radicals (**2**), while **9** is formed by recombination of radicals **2** and **3**. Dimerization of diphenylphosphonyl radicals affords two isomeric products (**12**, **13**). Similar dimerization modes have been reported for diethoxyphosphonyl radicals (see eq 10).³⁵ Although the addition of phosphonyl radicals to **1**



has been reported,¹¹ this reaction is expected to be unimportant at the low concentrations of substrate (0.005 M) employed in this study.

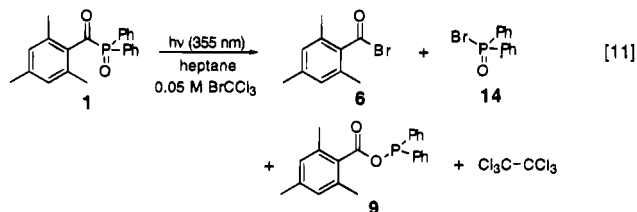
Steady-state infrared spectroscopy proved particularly useful for the identification of the carbonyl-containing products. Figure 6 shows the steady-state FTIR spectra recorded from photolysis of **1** in deoxygenated CH₂Cl₂ in the absence and presence of 0.05 M BrCCl₃. Photolysis (355 nm excitation) of a deoxygenated 0.005 M solution of **1** in the absence of added radical trap leads to a decrease in the carbonyl absorption of **1** at 1668 cm⁻¹ and growth of two carbonyl bands at 1697 and 1738 cm⁻¹ (Figure 6a). The 1697 cm⁻¹ band is assigned to overlapping absorptions of **10** and **11** while the band at 1738 cm⁻¹ is

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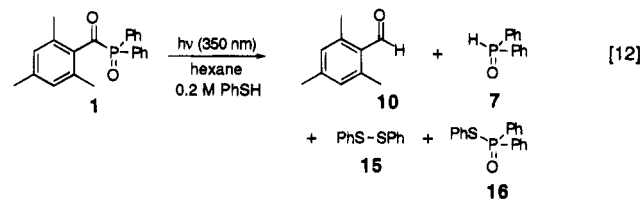
assigned to **9** on the basis of its similarity to the literature value.³² The band centered at 1605 cm⁻¹ changes only slightly in intensity during photolysis, and is assigned to phenyl ring stretches of **1** and the photolysis products.³⁶ Similar FTIR spectra were obtained from photolysis of **1** in deoxygenated *n*-heptane solution.

Photolysis (355 nm excitation) of deoxygenated 0.005 M solutions of **1** in *n*-heptane or CH₂Cl₂ in the presence of 0.05 M BrCCl₃ affords 2,4,6-trimethylbenzoyl bromide (**6**), diphenylphosphinic bromide (**14**), **9**, and hexachloroethane (see eq 11). The steady-state FTIR spectra of the crude photolysates



are shown in Figure 6b. The complete suppression of **10** and **11**, and the clean formation of **6** (1802 cm⁻¹) demonstrates that **2** was trapped quantitatively by BrCCl₃. The persistent formation of **9** (1738 cm⁻¹) under these conditions indicates that it is formed mainly via cage recombination of radicals **2** and **3** or, alternatively, via excited-state rearrangement of **1**. The carbonyl IR band assigned to **9** is formed within the response time of the TRIR detector (<50 ns) consistent with this conclusion. Furthermore, ³¹P CIDNP studies of **1** also indicate that **9** is formed by cage recombination of **2** and **3**.³³ Rapid geminate reaction of **2** and **3** may be facilitated by the large ³¹P hyperfine coupling constant (370 G) of the diphenylphosphonyl radical (**3**).^{5,12}

Finally, we have identified the products from photolysis of **1** in the presence of PhSH. GC and GC/MS analysis of the crude photolysate obtained from photolysis (350 nm) of deoxygenated 0.005 M solutions of **1** in hexane in the presence of 0.2 M PhSH showed the formation of **7** and **10**, the expected products of hydrogen atom abstraction from PhSH by radicals **2** and **3**. Phenyl disulfide (**15**) and diphenylphosphinic thiophenoxide (**16**) were also detected (see eq 12). (Benzoyloxy)phosphine **9** is presumably formed under these conditions but is not detected by GC techniques.



Summary and Conclusions

2,4,6-Trimethylbenzoyl (**2**) and diphenylphosphonyl (**3**) radicals, generated from photolysis of (2,4,6-trimethylbenzoyl)-diphenylphosphine oxide (**1**), have been detected directly by TRIR and LFP, respectively. Rate constants for reaction of the two radicals with BrCCl₃, PhSH, and Ph₂CHOH have been determined. Radicals **2** and **3** exhibit strikingly similar reactivities, with rate constants decreasing with increasing bond strength of the radical trap. Methyl substitution on the phenyl ring of the benzoyl radical causes a slight reduction in the rate of atom abstraction and a ca. 20 cm⁻¹ red shift in the carbonyl

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IR absorption. Steady-state studies have confirmed that radicals **2** and **3** react via atom abstraction from BrCCl_3 and PhSH. In addition to the expected free radical-derived products, photolysis of **1** affords diphenyl[(2,4,6-trimethylbenzoyl)oxy]phosphine (**9**) via cage recombination of **2** and **3**. Additional time-resolved spectroscopic studies of benzoyl and phosphonyl radicals are in progress.

Experimental Section

^1H and ^{31}P NMR spectra were recorded on a Bruker AF250 NMR spectrometer at 250 and 100 MHz, respectively. Gas chromatographic analyses were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector, a Hewlett-Packard 3392A integrator, and an HP-1 capillary column (25 m \times 0.2 mm; Hewlett-Packard, Inc.). GC/MS analyses were carried out using a Hewlett-Packard 5988A GC/MS system and a Hewlett-Packard 5890 gas chromatograph equipped with an HP-1 capillary column (25 m \times 0.2 mm; Hewlett-Packard, Inc.) and interfaced to a Hewlett-Packard 9133 data station. Ultraviolet absorption spectra were recorded on a Hewlett-Packard HP8452A UV spectrometer. Conventional infrared spectra were recorded on a Perkin-Elmer 1620 FTIR spectrometer.

Dichloromethane (Fisher) and *n*-heptane (Fisher) were distilled from calcium chloride and calcium hydride, respectively, under argon immediately prior to use. Benzhydrol (Aldrich) was sublimed before use. Hexane (Fisher HPLC), 2,4,6-trimethylbenzaldehyde (Aldrich), diphenylphosphinic chloride (Aldrich), diphenylphosphine oxide (Aldrich), bromotrichloromethane (Aldrich Gold Label), thiophenol (Aldrich Gold Label), and phenyl disulfide (Eastman Kodak) were used as received.

(2,4,6-Trimethylbenzoyl)diphenylphosphine oxide (**1**) obtained from BASF (Germany) was recrystallized from diethyl ether. Diphenyl-[(2,4,6-trimethylbenzoyl)oxy]phosphine (**9**) was synthesized³² from 2,4,6-trimethylbenzoic acid (Aldrich) and chlorodiphenylphosphine (Aldrich).

Time-resolved infrared experiments employed the pulses from a Quanta-Ray Nd-YAG laser (355 nm, 30 mJ/pulse, 7 ns) as the excitation source. The IR probe consisted of a Mütek MDS 1100 diode laser fitted with a Mütek MDS 1200 monochromator and sample chamber. Solutions were flowed continuously through a 2 mm path length gas

tight IR cell fitted with calcium fluoride windows. The TRIR system has been described in detail elsewhere.³⁷

Laser flash photolysis experiments employed the pulses (355 nm, ca. 10 mJ/pulse, 6 ns) from a Quanta-Ray DCR II Nd-YAG laser and a computer-controlled system which has been described elsewhere.³⁸ The current instrument employs a Tektronix TDS320 (100 MHz, 500 megasamples/s) digital oscilloscope in place of the Tektronix 7912 transient digitizer. Solutions of **1** were prepared at concentrations (~ 0.001 M) such that the absorbance at the excitation wavelength (355 nm) was ca. 0.3. Transient absorption spectra were recorded employing a flow system to ensure that a fresh volume of sample was irradiated by each laser pulse. Quenching rate constants were measured using argon-saturated static samples contained in 1 \times 1 cm Suprasil quartz cells. Fresh solutions were prepared at each quencher concentration.

Steady-state photolysis experiments were carried out in a Rayonet photochemical reactor equipped with two or four RPR-350 (350 nm) lamps or employed the pulses of the Nd-YAG laser (355 nm). Photolysis solutions were contained in 10 \times 100 mm Pyrex test tubes which were sealed with rubber septa or in the gas tight calcium fluoride IR cell. The solutions were deoxygenated prior to photolysis with a stream of dry argon. Photoproducts were identified by GC/MS, IR, NMR, and/or comparison with authentic samples.

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