

# Synthesis, Crystal Structures, and Laser Flash Photolysis of tert-Butyl Aroylperbenzoates<sup>1</sup>

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*tert*-Butyl aroylperbenzoates (1-7) were synthesized. Single-crystal structures for **2** and **5** show that the perester and benzophenone carbonyl groups are almost coplanar in each. Laser flash photolysis (LFP,  $\lambda_{ex} = 355$  nm) of 1–5 in CCl<sub>4</sub> produces the corresponding anoylphenyl radicals (9–13). The lifetimes of the para aroyl-substituted phenyl radicals (9–12) are similar ( $\sim$ 0.4  $\mu$ s), but each is shorter lived than the meta aroyl-substituted phenyl radical (13). LFP of 2, 6, and 7 also produces different (tert-butyldioxycarbonylbenzoyl)benzyl radicals (8, 14, and 15,  $\lambda_{max} \approx 320$ nm). The lifetimes of each in CCl<sub>4</sub> have been found to be  $\sim 17-18 \,\mu$ s. The effect of substituents on the quantum yield of decomposition of 1-7 and the lifetimes of 9-13 is discussed.

### Introduction

Although thousands of tons of vinyl polymers are made annually by diaroyl peroxide and peroxyester-catalyzed free-radical polymerization, peroxides are rarely used as photoinitiators, even when their bond homolysis reactions can be made efficient by sensitization. Photochemical processes involving aromatic ketones and either the Norish Type I cleavage or bimolecular electron transfer processes that produce radicals are generally used for photoinitiated monomer to polymer conversions.<sup>2</sup> tert-Butyl aroylperbenzoates (BP) are good candidates as initiators for photochemical vinyl polymerization because of the known direct dissociation of their weak -O-Obond. Their photochemical decomposition and activities as photoinitiators have been investigated.<sup>3,4</sup> They have been shown to be efficient photochemical sources of aroylbenzoyloxyl and aroylphenyl radicals.<sup>3,4</sup>

The kinetics of formation and decay of the singlet and triplet states of BPs have been studied by laser flash photolysis (LFP).<sup>5,6</sup> Lifetimes of their triplet states are less than  ${\sim}1$  ns.<sup>5,6</sup> The 550 nm absorption obtained from the 355 nm LFP (pulse width  $\sim$ 7 ns) of BPs has been

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assigned to the aroylphenyl radicals, and bimolecular rates of quenching of the 4-benzoylphenyl and 3-(4'methylbenzoyl)phenyl radicals by double-bond-containing monomers have been found to be in the range of  $10^{7}$ -10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>.<sup>6</sup>

The photochemical behavior of BPs containing one or two dissociable groups, e.g., tert-butyl 4-(4'-methylbenzoyl)perbenzoate (1) and tert-butyl 4-(4'-chloromethylbenzoyl)perbenzoate (2), has also been compared recently.<sup>7</sup> **2**, which has both C–Cl and perester groups conjugated with the benzophenone chromophore, produces not only the 4-(4'-chloromethylbenzoyl)benzoyloxyl and 4-(4'-chloromethylbenzoyl)phenyl radicals but also the benzyl-type radical [4-(4'-tert-butyldioxycarbonylbenzoyl)benzyl radical], the latter forming due to direct cleavage of the C-Cl bond.7

tert-Butyl 4-(3'-methylbenzoyl)perbenzoate (3), tertbutyl 4-(4'-bromobenzoyl)perbenzoate (4), tert-butyl 3-(4'methylbenzoyl)perbenzoate (5), tert-butyl 3-(4'-bromomethylbenzoyl)perbenzoate (6), and tert-butyl 3-(3'-bromomethylbenzoyl)perbenzoate (7) (Figure 1) were recently synthesized and studied. Herein we report quantum yields of dissociation of these BPs and the lifetimes of the corresponding aroylphenyl radicals obtained by LFP. We also present spectroscopic evidence for the formation of benzyl-type radicals and consider their lifetimes.

# **Results and Discussion**

Quantum Yields of Dissociation. BPs 1-7 show the characteristic  $n \rightarrow \pi^*$  transition of the benzophenone chromophore. Each has a maximum at  $\sim$ 350 nm in both benzene and CCl<sub>4</sub>. When irradiated at 350 nm, each produces similar products that are derived from the corresponding aroylbenzoyloxyl and aroylphenyl radicals.

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6.  $R_1 = Br \cdot CH_2$ ,  $R_2 = H$ 7.  $R_1 = H$ ,  $R_2 = Br - CH_2$ 

FIGURE 1. tert-Butyl aroylperbenzoates.

TABLE 1. Quantum Yields of Bond Dissociation  $(\phi_{diss})^a$ 

	$\phi_{ m diss}$	
BP	-0-0-	C-X
<b>1</b> <sup>b</sup>	0.82	
$2^{b}$	0.63	0.26
3	0.83	
4	0.87	
5	0.92	
6	0.33	0.49
7	0.43	0.39

<sup>*a*</sup> Intensity ( $I_0$ ) = 9.2 × 10<sup>16</sup> quanta L<sup>-1</sup> s<sup>-1</sup>; solvent = C<sub>6</sub>D<sub>6</sub>; concentration = 7.25-8.42 × 10<sup>-3</sup> M; error = within 10%. <sup>*b*</sup>Ref 7.

Thus, decomposition of 1-7 follows the general mechanism of homolytic dissociation of the perester bond due to the rapid intramolecular triplet energy dissipation.<sup>7</sup> In the case of BPs containing the CH<sub>2</sub>-X group (**2**, **6**, and **7**), dissociation of the C-X bond is also observed as indicated by formation of dehalogenated products.

The quantum yields of dissociation ( $\phi_{diss}$ ) of the perester and C-X bonds as measured in C<sub>6</sub>D<sub>6</sub> are presented in Table 1. The  $\phi_{diss}$  value of the perester bond of **5** was the highest among that of **1**-**7**. However, there are no major differences in the  $\phi_{diss}$  values for the perester cleavage of **1**-**5**, indicating that the  $\phi_{diss}$  of the perester bond is not significantly affected by the perester moiety. It makes little difference whether the perester is present at the para or meta position with respect to the benzophenone carbonyl group. Similarly, the position of the methyl group or even replacing the methyl group with a bromine atom has little or no influence on the  $\phi_{diss}$  of the perester bond.

The higher  $\phi_{\text{diss}}$  value observed for either the C–X bond or the perester bond is the limiting quantum yield of decomposition for **2**, **6**, and **7**.<sup>7</sup> The higher  $\phi_{\text{diss}}$  values of **6** and **7** are 0.49 and 0.43, respectively, which are much lower than that of other BPs. This indicates that their decomposition is a slow process. The  $\phi_{\text{diss}}$  values of the perester bond of **6** (0.33) and **7** (0.43) are also substantially lower than those of the other BPs. This is due to the presence of the benzylic bromide function, which has been found to decrease the  $\phi_{\text{diss}}$  of the perester bond.<sup>7</sup> A benzylic bromide function at either the para or meta position has a similar effect.



**FIGURE 2.** ORTEP drawings (50% probability ellipsoids) of **2** and **5**.

Decomposition of the  $CH_2$ -Br bond occurs preferentially to that of the perester bond. Consequently, because of the heavy-atom-induced cage radical pair recombination of the bromine atom with the benzyl-type radical, one observes a reduced  $\phi_{diss}$  of the perester bond in these molecules. The heavy atom may enhance the depopulation of the triplet state by inducing nonradiative decay of the triplet state,<sup>8</sup> and this may lower  $\phi_{diss}$  as observed in the case of 4-(bromomethyl)benzophenone.<sup>7</sup> However, this is ruled out in the case of the BPs. When bromine is present in a nondissociable form, the effect was not observed, as is reflected by the higher  $\phi_{diss}$  of the perester bond of **4**.

**Crystal Structures.** Photochemical dissociation of peroxides in the solid state has been the subject of various studies.<sup>9</sup> Although esters generated from *tert*-alkyl hydroperoxides are comparatively stable,<sup>10</sup> crystal structure data on peroxides and peresters are rather limited.<sup>11</sup> This is undoubtedly due to the decay that often occurs when their crystals are exposed to the X-ray radiation.<sup>12</sup> BPs **1**–**7** form high-quality crystal structures of **2** and **5** have been determined in order to assess the structural effect imparted by the perester moiety when it is present at the para or meta position with respect to the benzophenone carbonyl group.

The single-crystal structures of **2** and **5** with a labeling scheme of atoms are shown in Figure 2. They have been found to crystallize in different space groups. Crystals of **2** are monoclinic, space group  $C^2$ , while those of **5** are monoclinic, space group  $P^2(1)$ . The perester carbonyl group [C(14)-O(2)] assumes anti conformation with

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# SCHEME 1. Formation of Aroylphenyl and Benzyl-Type Radicals



respect to the benzophenone carbonyl group [C(7)-O(1)]in **2**, while the carbonyl groups assume syn conformation in **5**.

The geometry of the perester group is similar in both compounds with perester bond [O(3)-O(4)] distances of 1.473(4) Å in **2** and 1.465(3) Å in **5**. The dihedral angles between the two mean planes created by C(1)-C(7) and C(7)-C(13) have been found to be 49.1 and 130.2° in **2** and **5**, respectively. No short van der Waals contacts between molecules were observed. The shortest distance between the molecules of **2** is found to be 3.99 Å. The same for **5** is 6.14 Å, which is the distance of one of its unit cell dimensions.

The  $\phi_{\rm diss}$  values of the perester bond are 0.63 for **2** and 0.92 for **5** in benzene. The crystal structures show that the carbonyl and perester groups, as well as the aromatic ring between them [C(7)–O(1), C(8)–C(13), and C(14)–O(3)-O(4)], are almost planar in both **2** and **5**. The torsion angle between the two carbonyl groups has been found to be 22.2 and 12.9° in **2** and **5**, respectively. Although scission of the perester bond in solution occurs at the triplet excited-state manifold, planarity of the two carbonyl groups and the perester bond also explains why the intramolecular triplet energy dispersion is so facile in these molecules, leading to the higher  $\phi_{\rm diss}$  of the perester bond.<sup>13</sup>

**Laser Flash Photolysis.** The 355 nm LFP (pulse width  $\sim$ 7 ns, 19 mJ/pulse) of **1**–**4** in CCl<sub>4</sub> resulted in two absorption bands having maxima at 320 and 550 nm (Figures 3 and 4). The 550 nm band can be assigned to the corresponding aroylphenyl radicals (**9**–**12**, Scheme 1) since the 550 nm absorption bands obtained from the 355 nm LFP of *tert*-butyl 4-(benzoyl)perbenzoate and **5** have been assigned to the 4-benzoylphenyl and 3-(4'-methylbenzoyl)phenyl (**13**) radicals, respectively. Details on this assignment have been previously provided.<sup>6</sup>

The lifetimes of **9–13** recorded in CCl<sub>4</sub> are included in Table 2, and the rates of quenching  $(k_q)$  of two para radicals (**9** and **12**) by various quenchers are presented



**FIGURE 3.** Transient absorption spectra obtained from 355 nm laser flash photolysis of **1** ( $1.75 \times 10^{-3}$  M) in CCl<sub>4</sub>, recorded (•) 20 ns and ( $\bigcirc$ ) 2  $\mu$ s after the laser pulse. Inset: kinetic trace monitored at 550 nm (from  $1.18 \times 10^{-3}$  M **1** in CCl<sub>4</sub>).



**FIGURE 4.** Transient absorption spectra obtained from 355 nm laser flash photolysis of **4** ( $1.79 \times 10^{-3}$  M) in CCl<sub>4</sub>, recorded (•) 20 ns and ( $\bigcirc$ ) 2  $\mu$ s after the laser pulse. Inset: kinetic trace monitored at 550 nm (from  $1.29 \times 10^{-3}$  M **4** in CCl<sub>4</sub>).

in Table 3. The meta-centered radical (13) is longer lived than the para-centered radicals (9–12). However, there are no significant differences in the lifetimes of 9–12 in similar concentration ranges of the precursor BPs. The 4-benzoylphenyl radical also has a similar lifetime (0.41  $\mu$ s) in CCl<sub>4</sub>.<sup>6</sup> This may be because the substituents are too remote to impart an observable effect on such reactive radicals. The  $k_q$  values of 9 and 12 by 1,4-cyclohexadiene and by the precursor BPs have been observed to be in

<sup>(13)</sup> There may be considerable differences in the geometries of these molecules when they are in their solid state and in solution, especially because of the flexible nature of the appended perester moiety. However, the high quantum yield of O-O bond dissociation suggests that molecules assume appropriate geometries in their triplet states such that the activation energy in causing scission of the O-O bond is minimal. A flat geometry in their triplet states might be imagined in which case triplet energy dissipation may be very facile. Density functional theory (DFT) calculations on some of these molecules are in the process of being carried to obtain information about the structure of their triplet states.

 TABLE 2.
 Lifetimes (r) of Aroylphenyl Radicals

 (Solvent = CCl<sub>4</sub>)

radical	precursor BP (concentration, M)	$ au, \mu \mathbf{s}$
9	$1.18 imes 10^{-3}$	0.44 (±0.01)
10	$1.77 imes10^{-3}$	$0.43 (\pm 0.01)$
11	$1.27 imes10^{-3}$	$0.34 (\pm 0.01)$
12	$1.29 imes10^{-3}$	$0.39 (\pm 0.01)$
<b>13</b> <sup>a</sup>	$1.41  imes 10^{-3}$	$0.62(\pm 0.02)$
<b>13</b> <sup>a</sup> <sup>a</sup> Ref 6.	$1.41  imes 10^{-3}$	0.62 (±0.02

 TABLE 3. Rate Constants (kq) of Quenching of the

 4-(4'-Methylbenzoyl)phenyl (9) and

 4-(4'-Bromobenzoyl)phenyl (12) Radicals<sup>a</sup>

	$k_{ m q} imes 10^9$ , ${ m M}^{-1}~{ m s}^{-1}$	
quencher	9	12
oxygen	1.34 (±0.03)	0.88 (±0.04)
1,4-cyclohexadiene	$1.13 (\pm 0.04)$	$1.14 (\pm 0.06)$
precursor BP	$1.59(\pm 0.10)$	0.87 (±0.03)

<sup>a</sup> Solvent = CCl<sub>4</sub>; concentration of precursor BPs was between  $8.44 \times 10^{-4}$  and  $2.65 \times 10^{-3}$  M.

the range of  $0.87-1.59 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . Similar values of  $k_q$  have been obtained for the 4-benzoylphenyl radical and **5**.<sup>6</sup> The rate constant of quenching of a photochemically generated phenyl radical<sup>14</sup> by the precursor benzoyl peroxide has been found to be  $2.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , and this is lower than our values. H-abstraction by the aroylphenyl radicals from the precursor BPs seems to be the likely reason for this.

In addition to a fast-decaying component, a slowdecaying component was also observed at 320 nm from LFP of all BPs except 4. In the case of 1 and 2, the slowdecaying components showed identical lifetimes ( $\tau \approx 17$  $\mu$ s), indicating that they belong to an identical transient that can be obtained from both 1 and 2. This  $\sim$ 320 nm absorption has been assigned to the corresponding benzyl-type radicals [4-(4'-tert-butyldioxycarbonylbenzoyl)benzyl) 8, 3-(4'-tert-butyldioxycarbonylbenzoyl)benzyl 14, and 3-(3'-tert-butyldioxycarbonylbenzoyl)benzyl 15] on the basis of the following facts: (a) the benzyl radical has a known absorption at 320 nm,<sup>15</sup> (b) the half-life time of a similar benzyl radical has been reported to be 10  $\mu$ s,<sup>16</sup> and (c) no slow-decaying component was observed at 320 nm from LFP of tert-butyl (4-benzoyl)perbenzoate and 4, which do no have methyl or CH<sub>2</sub>-X groups.



The assignment is further supported in that in optically matched experiments, the optical density of the slow-decaying component at 320 nm was found to be



**FIGURE 5.** Traces at 320 nm obtained from the 355 nm laser flash photolysis of **1** and **2**; initial absorbance of both BPs at 355 nm = 0.33.

TABLE 4.Lifetimes (7) of Benzyl-Type Radicals(Solvent = CCl4)

radical	precursor BP (concentration, M)	τ, μ <b>s</b>
8	$1.77 imes10^{-3}$	16.96 (±1.07)
14	$1.51 imes10^{-3}$	17.05 (±1.18)
15	$2.29 imes10^{-3}$	18.13 (±2.25)

higher for **2** than for **1** (Figure 5). This is as expected, since 8 forms directly due to cleavage of the C-Cl bond in the case of **2**, while in the case of **1**, it forms when different radicals abstract an H-atom from the methyl group. Similar observations were made in the case of 5 and 6 where 14 forms directly due to scission of the C-Br bond from 6. The lifetimes of 8, 14, and 15 have also been found to be similar. The same resonance factor is available to stabilize these radicals. Each was guenched by oxygen, as was the fast-decaying component at the 320 nm. The rate of quenching of these radicals could not be obtained because of the interference of the fast-decaying component. We also observed no measurable signal at 550 nm during LFP of either 6 or 7 where formation of **14** or **15**, respectively, is competitive and predominates. Investigation of the photopolymerization initiation activities of some of these BPs is underway.

# Conclusions

In the photodecomposition of 1-5, the  $\phi_{diss}$  of the perester bond was found to be the highest for 5. This compound has the perester moiety positioned meta with respect to the benzophenone carbonyl group. However, neither the position of the methyl group nor the replacement of the methyl group with a bromine atom showed any significant effect on the  $\phi_{\text{diss}}$  of the perester bond as reflected by similar values of the  $\phi_{diss}$  of **1**–**4** in benzene. Single-crystal structures show that the carbonyl and perester groups assume anti conformation in 2, while syn confirmation is observed in 5. The carbonyl and perester groups, as well as the aromatic ring separating them, are almost planar in both 2 and 5. The presence of a benzylic bromide function either at the para or meta position significantly lowers the  $\phi_{\rm diss}$  of the perester bond. This is supported by LFP studies. The 355 nm LFP of 1-5 produced the corresponding aroylphenyl radicals (9-13,

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 $\lambda_{\rm max}$  550 nm). The lifetimes of para radicals (9–12) measured in 1.18–1.77  $\times$  10<sup>-3</sup> M solution of 1–4 in CCl<sub>4</sub> have been found to be  $\sim 0.4 \ \mu s$ , which is lower than the lifetime of the meta radical (13  $\sim$ 0.62  $\mu$ s, 1.41  $\times$  10<sup>-3</sup> M 5 in CCl<sub>4</sub>). The 550 nm absorption of the aroylphenyl radicals was not observed from LFP of 6 and 7 in which formation of benzyl-type radical (14 and 15) predominates. The lifetimes of the benzyl-type radicals (8, 14, and 15,  $\lambda_{max} \approx$  320 nm) in CCl<sub>4</sub> have been found to be  $\sim 17 - 18 \ \mu s.$ 

# **Experimental Section**

Reagents and solvents were obtained from commercial suppliers and used as received unless otherwise noted. Solvents used for syntheses, e.g., benzene, toluene, and cyclohexane were dried over sodium/benzophenone under argon before use. Column chromatography and thin-layer chromatography (TLC) were performed using standard-grade silica gel (32–63  $\mu$ m, 60 Å) and silica gel plates (200  $\mu$ m). Melting points are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded on 200 and 400 MHz spectrometers. CDCl<sub>3</sub> was the solvent for NMR unless otherwise noted, and chemical shifts are reported in parts per million (ppm) for <sup>1</sup>H NMR on the  $\delta$ scale relative to TMS at 0.0 ppm. GC/MS data were collected using spectrometers having 30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m columns. The  $\phi_{diss}$  values were determined by <sup>1</sup>H NMR using C<sub>6</sub>D<sub>6</sub> as the solvent and hexamethylsiloxane as the internal standard. The detailed procedure has been reported previously.7 Product analyses were done using GC/MS as described previously.<sup>7</sup>

Synthesis. The synthesis of 1 and 2 has been reported earlier.<sup>7</sup> 3-7 have been synthesized following the general method of synthesis of peresters from their corresponding aroylbenzoic acids (16-19).17-20 A detail of synthesis and purification methods of BPs 3-7 and their spectroscopic data, as well as synthesis of 16-19, has been provided in Supporting Information.

X-ray Crystallography. Data collection was performed at room temperature with Mo K $\alpha$  using a Bruker AXS SMART platform diffractometer.<sup>21</sup> Intensity data were collected using three different  $\phi$  settings and 0.3° increment  $\omega$  scans,  $2\theta <$ 56.58° for **2** and  $2\theta < 56.56^\circ$  for **5**, which corresponds to more than a hemisphere of data. The SAINT<sup>21</sup> program was used

for data integration, and corrections for absorption and decay were carried out using the SADABS program.<sup>22</sup> The X-ray structures were determined by direct methods,<sup>23</sup> and refinement was done by full matrix least squares  $^{22}$  on  $F^2$  using all 3549 unique data for 2 and 3558 unique data for 5. The refinement included anisotropic thermal parameters for nonhydrogen atoms with isotropic thermal parameters for all hydrogen atoms. In the case of 2, anomalously large thermal parameters were observed as a result of two alternative orientations for the C-atoms of the tert-butyl group. Similar statistical disorder has been previously observed for the crystal structure of 2,4,6-tri-*tert*-butylperbenzoate.<sup>11</sup> Although these data were collected at room temperature, such statistical disorder was not observed in the case of 5. The final refinement converged to  $wR_2 = 0.1592$  (for  $F^2$ , all data) and  $R_1 = 0.0642$ [*F*, 2558 reflections with  $I > 2\sigma(I)$ ] in the case of **2** and w $R_2 =$ 0.1142 (for  $F^2$ , all data) and  $R_1 = 0.0516$  [F, 2582 reflections with  $I > 2\sigma(I)$  in the case of 5

Laser Flash Photolysis. Nanosecond flash photolysis studies were performed using a kinetic spectrometric detection system previously described.<sup>24</sup> The excitation pulse (355 nm, 19 mJ/pulse) was the third harmonic of a Q-switched Nd:YAG laser. The excitation pulse width was  $\sim$ 7 ns. Transients produced were followed temporally and spectrally by a computer-controlled kinetic spectrophotometer. The sample solutions showing an absorbance in the range of 0.15-0.35 at the excitation wavelength in 1 cm<sup>2</sup> quartz cuvettes were used and degassed continuously with argon during experiments. Fresh samples were used for obtaining each kinetic trace. Twicedistilled CCl<sub>4</sub> was used as the solvent for LFP. The  $k_{\alpha}$  values were calculated by monitoring the lifetimes at 550 nm and plotting 1/lifetime against the concentration of quenchers.

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Supporting Information Available: Experimental details of synthesis and purification and spectral data of BPs 3-7, synthetic procedures of 16-19, <sup>1</sup>H and <sup>13</sup>C NMR of 3-7, UV-vis spectra of 1-7, X-ray crystal structure data of 2 and 5, and various kinetic traces and fittings for lifetimes and rate constants. This material is available free of charge via the Internet at http://pubs.acs.org.

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