# Effect of Ring Substitution on the Photochemistry of $\alpha$ -(Aryloxy)acetophenones<sup>†</sup>

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The photochemistry of a series of 10  $\alpha$ -(aryloxy)acetophenones has been examined by quantum yield, product studies, and laser flash photolysis techniques. Triplet decay involves a competition of  $\beta$ -cleavage with intramolecular quenching by the  $\beta$ -aryl group, the latter being favored in all systems. Typical triplet lifetimes at room temperature range from 60 to 260 ps and are rather insensitive to the substitution pattern.  $\beta$ -Cleavage rate constants range between  $1 \times 10^7$  and  $3 \times 10^9$  s<sup>-1</sup> and are strongly favored by electron releasing substituents, such as 4-methoxy. The determination of true quantum yields of  $\beta$ -cleavage requires the addition of thiophenol as a radical trap to prevent the efficient back reaction that takes place otherwise; under these conditions quantum yields range from  $10^{-3}$  to 0.14, the highest value being obtained for the 4-methoxy and 4-hydroxy derivatives.

### Introduction

Ketones having suitable substituents in the  $\alpha$ -position (i.e.  $COCH_2X$ ) can readily undergo photochemical homolytic  $\beta$ -cleavage leading to free radicals. Several moieties have been reported to be good leaving groups in this type of reaction; for example; literature reports include sulfonates,<sup>1</sup> halogens,<sup>2,3</sup> phenoxyl,<sup>4-7</sup> and thiophenoxyl<sup>8-17</sup> radicals. In fact, it is rather interesting that these last two examples would undergo fragmentation, since this reaction occurs in competition with remarkable efficient carbonyl deactivation by the  $\beta$ -phenyl ring.<sup>18</sup> In the case of  $\alpha$ phenoxyacetophenone (Ia; X = H), we have shown that cleavage (reaction 1) occurs with a quantum yield of 0.004 in benzene,<sup>6</sup> where intramolecular deactivation has a rate constant of ca.  $8 \times 10^9$  s<sup>-1</sup>.



Intramolecular deactivation has been shown to involve the conformation shown below; the process is about 1 order of magnitude more rapid in Ia than in  $\beta$ -phenylpropiophenone (II),<sup>19</sup> reflecting the change in nonbonded interactions.



In this paper we report the results of a study of the kinetics and quantum yields for the photochemistry of an extensive series of  $\alpha$ -(aryloxy)acetophenones. Our work involves a combination of laser flash photolysis, quantum yield, phosphorescence, and product studies.

#### **Experimental Section**

Materials. The solvents benzene (Aldrich), dichloromethane (Fisher), methylcyclohexane (Aldrich), isopentane (Aldrich), ethyl ether (Fisher), and ethanol (Aldrich) were used as received and were all spectrograde.

1-Methylnaphthalene (Aldrich) was vacuum distilled, and thiophenol (Aldrich) was used as received.

The ketones Ia-j were synthesized by reaction of  $\alpha$ -chloroacetophenone with the corresponding phenol using ethanol as solvent in alkaline media.<sup>20</sup> Physical and spectrometric data for the ketones under study are listed below.

α-Phenoxyacetophenone (Ia): mp 71–72 °C (lit.<sup>21</sup> mp 71–72 °C); NMR ( $\dot{C}DCl_3$ )  $\delta$  5.20 (s, 2 H), 6.80–8.20 (m, 10 H); MS m/z(%) 212 (16, M<sup>+</sup>), 106 (9), 105 (100), 77 (51), 65 (74), 51(21). Anal. Found: C, 79.36; H, 5.67. Calcd. for C<sub>14</sub>H<sub>12</sub>O<sub>2</sub>: C, 79.22; H, 5.70.

α-(3-Methylphenoxy)acetophenone (Ib): mp 74-75 °C (lit.4a mp 72 °C); NMR (CDCl)<sub>3</sub>) δ 2.33 (s, 3 H), 5.21 (s, 2 H), 6.65-8.20 (m, 9 H); MS m/z (%) 226 (9, M<sup>+</sup>), 121 (1.5), 105 (100), 77 (45), 65 (19), 51 (20). Anal. Found: C, 79.78; H, 6.21. Calcd for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>: C, 79.62; H, 6.23.

α-(4-Methylphenoxy)acetophenone (Ic): mp 65-66 °C (lit.4

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 Table I. Product Distribution Obtained upon Lamp

 Photolysis of 0.05 M Ketones in Benzene

|                           | % product distribution |         |                     |   |  |
|---------------------------|------------------------|---------|---------------------|---|--|
| substrate/<br>substituent | aceto-<br>phenone      | phenolª | deoxy-<br>benzoinsª | PhCOCH <sub>2</sub> -<br>CH <sub>2</sub> COPh |  |
| Ia/H                      | 25.8                   | 38.0    | 26.9                | 9.3   |  |
| Ib/3-Me                   | 24.7                   | 41.2    | 21.7                | 12.4  |  |
| Ic/4-Me                   | 22.1                   | 42.9    | 13.8                | 21.2  |  |
| Id/4-MeO                  | 33.2                   | 32.3    | 16.7                | 17.9  |  |
| Ie/3-OH                   | 44.6                   | 42.5    | 12.8                | b   |  |
| If/4-OH                   | 39.1                   | 37.6    | 14.5                | 8.9   |  |
| Ig/3-Cl                   | 23.8                   | 34.2    | 42.1                | Ь   |  |
| Ih/4-Cl                   | 32.1                   | 31.3    | 36.7                | b   |  |
| Ii/4-CN                   | 46.8                   | 53.2    | b                   | b   |  |
| Ij/4-CO <sub>2</sub> Me   | 34.8                   | 65.2    | b                   | Ь   |  |

<sup>a</sup> Appropriately substituted. <sup>b</sup> Less than 0.5%.

mp 56 °C); NMR (CDCl<sub>3</sub>)  $\delta$  2.25 (s, 3 H), 5.21 (s, 2 H), 6.73–8.20 (m, 9 H); MS m/z (%) 226 (11, M<sup>+</sup>), 121 (2), 105 (100), 77 (45), 65 (17), 51 (19). Anal. Found: C, 79.81; H, 6.29. Calcd for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>: C, 79.62; H, 6.23.

α-(4-Methoxyphenoxy)acetophenone (Id): mp 66–67 °C (lit.<sup>4a</sup> mp 69 °C); NMR (CDCl<sub>3</sub>) δ 3.73 (s, 3 H), 5.21 (s, 2 H), 6.80–8.20 (m, 9 H); MS m/z (%) 242 (52, M<sup>+</sup>), 123 (13), 105 (100), 77 (41), 65 (1), 51 (15). Anal. Found: C 74.19; H, 5.69. Calcd for C<sub>15</sub>H<sub>14</sub>O<sub>3</sub>: C, 74.36; H, 5.82.

 $\alpha$ -(3-Hydroxyphenoxy)acetophenone (Ie): mp 141-142 °C; NMR (CDCl<sub>3</sub>)  $\delta$  5.24 (s, 2 H), 6.50-8.05 (m, 9 H); MS m/z (%) 228 (<1%, M<sup>+</sup>), 105 (100), 77 (32), 65 (5), 51 (7). Anal. Found: C, 73.90; H, 5.09. Calcd for C<sub>14</sub>H<sub>12</sub>O<sub>3</sub>: C, 73.67; H, 5.30.

α-(4-Hydroxyphenoxy)acetophenone (If): mp 179–180 °C; NMR (CDCl<sub>3</sub>) δ 5.20 (s, 2 H), 6.80–8.10 (m, 9 H); MS m/z (%) 228 (45, M<sup>+</sup>), 105 (100), 77 (37), 65 (16), 51 (16). Anal. Found: C, 73.75; H, 5.21. Calcd for C<sub>14</sub>H<sub>12</sub>O<sub>3</sub>: C, 73.67; H, 5.30.

α-(3-Chlorophenoxy)acetophenone (Ig): mp 93–94 °C (lit.<sup>4a</sup> mp 96.5 °C); NMR (CDCl<sub>3</sub>) δ 5.21 (s, 2 H), 6.95–8.20 (m, 9 H); MS m/z (%) 248 (1.4, M<sup>+</sup> + 2), 246 (4.6, M<sup>+</sup>), 105 (100), 77 (46), 65 (6), 51 (21). Anal. Found: C, 68.27; H, 4.38; Cl, 14.57. Calcd for C<sub>14</sub>H<sub>11</sub>ClO<sub>2</sub>: C, 68.16; H, 4.49; Cl, 14.37.

 $\alpha$ -(4-Chlorophenoxy)acetophenone (Ih): mp 98–99 °C (lit.<sup>4a</sup> mp 99.5 °C); NMR (CDCl<sub>3</sub>)  $\delta$  5.20 (s, 2 H), 6.80–8.20 (m, 9 H): MS m/z (%) 248 (1.8, M<sup>+</sup> + 2), 246 (5.1, M<sup>+</sup>), 105 (100), 77 (47), 65 (6), 51 (21). Anal. Found: 67.99; H, 4.31; Cl, 14.36. Calcd for C<sub>14</sub>H<sub>11</sub>ClO<sub>2</sub>: C, 68.16; H, 4.49; Cl, 14.37.

α-(4-Cyanophenoxy)acetophenone (Ii): mp 160–161 °C; NMR (CDCl<sub>3</sub>) δ 5.18 (s, 2 H), 6.80–8.10 (m, 9 H); MS m/z (%) 237 (7, M<sup>+</sup>), 105 (100), 77 (35), 65 (4), 51 (16). Anal. Found: C, 75.83; H, 4.51; N, 5.90. Calcd for  $C_{15}H_{11}NO_2$ : C, 75.93; H, 4.67; N, 5.90.

 $\alpha$ -(4-Carbomethoxyphenoxy)acetophenone (Ij): mp 117-118 °C; NMR (CDCl<sub>3</sub>)  $\delta$  3.86 (s, 3 H), 5.33 (s, 2 H), 6.85-8.10 (m, 9 H); MS m/z (%) 270 (4.9, M<sup>+</sup>), 239 (1.8), 105 (100), 77 (37), 65 (6), 51 (12). Anal. Found: C, 71.28; H, 5.03%. Calcd for C<sub>16</sub>H<sub>14</sub>O<sub>4</sub>: C, 71.10; H, 5.22.

General Techniques. UV-vis spectra were recorded with a HP-8451A diode array spectrometer. Phosphorescence spectra were recorded with a Perkin-Elmer LS5 spectrofluorimeter equipped with a PE-3600 data station.

GC analysis were carried out on a Perkin-Elmer Model 8320 capillary gas chromatograph employing a 12 m J & W bonded phase vitreous silica BP1 silicone column. GC-MS analysis were performed in a Hewlett-Packard Model 5995 system.

Proton NMR spectra were recorded at the University of Ottawa with a Varian 200-MHz instrument. Melting points were determined in a Mel-Temp apparatus and were not corrected.

**Product Studies and Quantum Yield Determinations.** Typical samples were 1 mL containing 0.05 M ketone in benzene or dichloromethane and were deaerated by bubbling oxygen-free nitrogen. The samples were containing in Pyrex tubes and were irradiated in a "merry-go-round" with 12 RPR-3000 lamps. The products were characterized and measured against authentic samples by GC and GC-MS. Dodecane was employed as an internal standard.

For the quantum yield determinations, the photofragmentation of valerophenone in benzene was employed as an actinometer,

Table II. Phosphorescence Data and Triplet Energies at 77 K

| ketone | substituent  | glass <sup>a</sup> | λ <sub>0,0</sub> | $E_{\rm T}$ , kcal/mol |
|--------|--------------|--------------------|------------------|------------------------|
| Ia     | Н            | EPA                | 394.7            | 72.5                   |
| Ib     | 3-Me         | MCH-IP (1:1)       | 409.1            | 70.0                   |
| Ic     | 4-Me         | MCH-IP (1:1)       | 408.1            | 70.0                   |
| Id     | 4-OMe        | EPA                | 394.4            | 72.5                   |
| Ie     | 3- <b>OH</b> | EPA                | 395.0            | 72.4                   |
| If     | 4-OH         | EPA                | 395.4            | 72.3                   |
| Ig     | 3-CI         | EPA                | 396.4            | 72.1                   |
| Īĥ     | 4-Cl         | EPA                | 395.0            | 72.3                   |
| Ii     | 4-CN         | EPA                | 393.0            | 72.8                   |
| Ij     | $4-CO_2Me$   | EPA                | 394.7            | 72.5                   |

<sup>a</sup>Abbreviations: MCH = methylcyclohexane; IP = 2 methylbutane; EPA = ethanol-2-methylbutane-ether, 2:5:5.

taking the quantum yield of acetophenone formation as  $0.30.^{22}$ 

Experiments were carried out in the absence and presence of thiophenol. In its absence, the total yield of irreversible photocleavage was based on all the products derived from the phenacyl radical (acetophenone, 1,4-diphenyl-1,4-butadione, and substituted deoxybenzoins). Table I provides the product distribution obtained in each case; mass balances were better than 90%. In the presence of thiophenol only the peak area corresponding to acetophenone was used, since under these conditions the radicals PhCOCH<sub>2</sub> are almost quantitatively trapped by the thiol. In fact thiophenol prevents the back reaction to such an extent that quantum yields in its presence are considerably higher than in its absence (vide infra).

Laser Flash Photolysis. Samples were contained in cells constructed of  $3 \times 7 \text{ mm}^2$  rectangular Suprasil tubing, and were deaerated by bubbling with oxygen-free nitrogen. The samples were irradiated with the pulses ( $337 \text{ nm}, \sim 8 \text{ ns}, \leq 10 \text{ mJ/pulse}$ ) from a Molectron UV-24 nitrogen laser. The signals from an RCA-4840 photomultiplier were initially captured by an R-7912 Tektronix transient digitizer and then transferred to a PDP11/23<sup>+</sup> computer that controlled the experiment and provided suitable storage, processing and hard copy capabilities. Transient absorption spectra were recorded either by a point-by-point method based on the decay traces obtained at each wavelength or with a gated intensified optical multichannel analyzer from EG & G. Further details on our laser equipment have been reported elsewhere.<sup>23</sup>

## Results

**Spectroscopic Properties.** The 77 K phosphorescence spectra of ketones Ia-j (see Table II) show vibrational structure characteristic of the  $n\pi^*$  triplet state of carbonyl compounds. Typical triplet energies are around 72 kcal/mol. The presence of polar ring substituents in the phenoxy group does not appear to affect the spectroscopic properties of the benzoyl chromophore. Table II shows the substitution pattern and phosphorescence data for the ketones under study.

**Product Studies and Quantum Yield Determinations.** Irradiation of ketones Ia-j leads to the formation of several products that can be attributed to initial  $\beta$ cleavage leading to phenacyl and substituted phenoxyl radicals. These radicals can undergo back reaction to generate the starting materials, abstract hydrogen, or undergo disproportionation and various radical-radical coupling reactions, among them ortho and para coupling (see Table I). Scheme I shows a summary of the productforming reactions illustrated for the case of Ic (where para substitution prevents the formation of para coupling products) along with their relative yields. The relative yields of products have already been reported for Ia<sup>6</sup> and are given for all substrates in Table I.

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| Table III. Kinetic Data <sup>a</sup> for Ketones Ia–j |             |                             |   |                         |                          |   |  |  |  |
|---|-------------|-----------------------------|---|-------------------------|--------------------------|---|--|--|--|
| ketone  | substituent | $\Phi_{eta	ext{-cleavage}}$ | $\Phi^{\mathrm{PhSH}}_{eta	ext{-cleavage}}$ | $k_q \tau_T^{b} M^{-1}$ | $\tau_{\mathrm{T}}$ , ps | $k_{\rm r} \times 10^{-8},  {\rm s}^{-1}$ |  |  |  |
| Ia  | Н           | 0.0030                      | 0.014                                       | 0.61                    | 122                      | 1.16                                      |  |  |  |
| Ib  | 3-Me        | 0.0010                      | 0.018                                       | 0.75                    | 150                      | 1.22                                      |  |  |  |
| Ic  | 4-Me        | 0.0020                      | 0.069                                       | 1.27                    | 254                      | 2.9                                       |  |  |  |
| Id  | 4-OMe       | 0.037                       | 0.14  | 1.66°                   | 166                      | 9.8                                       |  |  |  |
| Ie  | 3-OH        | 0.014                       | 0.023                                       | 1.65                    | 165                      | 1.43                                      |  |  |  |
| If  | 4-OH        | 0.031                       | 0.14  | $0.60^{d}$              | 60                       | 27.2                                      |  |  |  |
| Ig  | 3-Cl        | 0.0010                      | 0.0014                                      | 0.68                    | 136                      | 0.10                                      |  |  |  |
| Iĥ  | 4-C1        | 0.0016                      | 0.016                                       | 1.23                    | 246                      | 0.67                                      |  |  |  |
| Ii  | 4-CN        | 0.00035                     | 0.0039                                      | $1.41^{b}$              | 141                      | 0.28                                      |  |  |  |
| Ij  | $4-CO_2Me$  | 0.00015                     | 0.0026                                      | 1.04                    | 208                      | 0.13                                      |  |  |  |

<sup>a</sup> In benzene, at room temperature, unless otherwise indicated. <sup>b</sup> Typical error  $\pm 20\%$ . <sup>c</sup> In CH<sub>2</sub>Cl<sub>2</sub>. <sup>d</sup>  $k_q = 5 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> for benzene and  $1.0 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup> for CH<sub>2</sub>Cl<sub>2</sub>.



The addition of a good hydrogen donor, such as thiophenol ( $\sim 0.02$  M) increases dramatically the yield of acetophenone and of the substituted phenol at the expense of the other products. It also prevents the back reaction leading to the starting material, which leads to a considerable increase in the quantum yield of products derived from a  $\beta$ -cleavage process.<sup>7</sup>

Quantum yield determinations, in the presence or absence of thiophenol, were carried out using the formation of acetophenone from valerophenone as an actinometer ( $\Phi$ = 0.30 in benzene),<sup>22</sup> and the values obtained are listed in Table III. We also include in this table the Stern-Volmer constants ( $k_q \tau_T$ ) determined in laser flash photolysis experiments, from which we can estimate the triplet lifetimes,  $\tau_T$  (vide infra).

Laser Flash Photolysis Studies. The triplet lifetime for  $\alpha$ -phenoxyacetophenones is generally too short to be determined directly with nanosecond techniques at room temperature.<sup>6</sup> Thus, we have employed a Stern–Volmer type of approach in these measurements, employing 1methylnaphthalene (MN) as a triplet quencher. These experiments lead to the formation of the readily detectable triplet state of the quencher (MN\*) as a consequence of triplet energy transfer from the excited ketone according to reaction 2.

$$I^* + MN \xrightarrow{R_q} I + MN^*$$
 (2)

This technique has been widely used in the characterization of short-lived triplet states. $^{6,19,24,25}$  Briefly, the



Figure 1. Representative plots according to eq 3 for the quenching of several  $\alpha$ -phenoxyacetophenones by 1-methylnaphthalene.

transient absorption from triplet 1-methylnaphthalene (MN\*) can be readily monitored in the 420-nm region. These absorptions (monitored before significant decay of MN\* takes place) are related to the Stern-Volmer constant according to equation 3. where  $A_{420}$  is the transient ab-

$$\frac{1}{A_{420}} = \alpha + \frac{\alpha}{k_{\rm q} \tau_{\rm T}[\rm MN]} \tag{3}$$

sorption at 420 nm,  $\tau_{\rm T}$  the triplet lifetime,  $k_{\rm q}$  the quenching rate constant (reaction 2) and  $\alpha$  a constant that incorporates experimental factors as well as the intersystem crossing efficiency for the substrate. Representative quenching plots are illustrated in Figure 1. The errors in these measurements are almost entirely derived from the uncertainty in the intercept in plots such as those in Figure 1; typical errors in  $k_{\rm q}\tau_{\rm T}$  are around 20%.

A further complication is present in the cases of 4methoxy- and 4-hydroxy-substituted  $\alpha$ -phenoxyacetophenones (Id and If). Laser excitation of these ketones leads to the formation of the corresponding phenoxyl radicals in good yields (see Table III and Scheme I), showing absorption maxima in the 400-nm region and consequently contribute to some extent to the absorption at 420 nm in the 1-methylnaphthalene quenching experiments. The values of transient absorption for these two examples were therefore corrected by subtracting the contribution due to phenoxyl radicals from the total value

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b

of  $A_{420}$ . The values of  $k_q \tau_T$  obtained in these measurements are listed in Table III.

#### Discussion

The data in Table II show unequivocally that the triplet states of Ia-j are all of the same type and not unlike that of acetophenone. The differences in behavior must therefore be the result of the different substitution patterns on the aryloxy group.

From the data in Table III it is possible to derive values of  $\tau_{\rm T}$  if a reasonable value of  $k_{\rm q}$  can be assumed. Further, if we assume that the short value of  $\tau_{\rm T}$  is determined by the competition between chemical  $(k_r)$  and nonchemical  $(k_{\rm d})$  decay pathways it is possible to derive values for these two components. Thus we assume that

$$\tau_{\mathrm{T}}^{-1} = k_{\mathrm{r}} + k_{\mathrm{d}} \tag{4}$$

where

$$I^* \xrightarrow{k_d} I$$
 (5)

I\* 
$$\xrightarrow{\alpha_r}$$
 products from  $\beta$ -cleavage (6)

Thus, if we assume that in the presence of thiophenol reaction 6 is not followed by back reaction to regenerate I,

$$\Phi_{\beta\text{-cleavage}} = \Phi_{\text{ISC}} \frac{k_{\text{r}}}{k_{\text{r}} + k_{\text{d}}} = \Phi_{\text{ISC}} k_{\text{r}} \tau_{\text{T}}$$
(7)

where  $\Phi_{ISC}$  is the quantum yield of intersystem crossing, which for aromatic ketones is frequently close to 1.0. This analysis leads to the values of  $k_r$  given in Table II, which are based on the assumption of values of  $5 \times 10^9$  and  $1 \times$  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$  for  $k_q$  in benzene and dichloromethane, respectively.

It is interesting to note that just as in the case of  $\beta$ arylpropiophenones examined earlier,<sup>19</sup> the values of  $k_d$ (which contribute >80% to  $\tau_{T}^{-1}$ ) do not fluctuate much in spite of the wide range of substituents examined. We propose that the explanation for this is that  $k_d$  is largely determined by the rate of conformational change leading to a geometry favorable for intramolecular quenching; while this quenching process may indeed involve charge transfer, the electron donor/acceptor characteristics of the ring are not reflected in the mobility of this group. The values of  $k_d$  for  $\alpha$ -(aryloxy)acetophenones are about 1 order of magnitude faster than for  $\beta$ -arylpropiophenones<sup>19</sup> as a result of reduction of nonbonded interactions (i.e. CH<sub>2</sub> eclipsing) due to the presence of an oxygen bridge in I.

The data in Table III clearly show that electron-donor substituents in I greatly enhance the efficiency and rate of  $\beta$ -cleavage by stabilizing the corresponding phenoxyl radical. A Hammett plot of  $k_r$  against  $\sigma^+$  (Figure 2) gives a good correlation ( $r^2 = 0.95$ ) with  $\rho = -1.53$ . Interestingly (but not surprisingly), the values of k, correlate moderately well with the rate constants for intermolecular hydrogen atom abstraction by *tert*-butoxyl from the corresponding phenols, i.e.



Thus, a plot of  $\log k_8$  vs  $\log k_r$  (not shown) has a slope of 1.33 ( $r^2 = 0.89$ ), where the values of  $k_8$  were taken from an earlier report.<sup>26</sup>



**Figure 2.** Hammett plot of  $\beta$ -cleavage rate constants  $(k_r)$  against

The values of  $k_r$  are remarkably high, typically in the  $10^7$  to >10<sup>9</sup> s<sup>-1</sup> range, and it is only the high efficiency of the deactivation process  $(k_d)$  that limits the quantum yields, particularly in systems with electron-withdrawing substituents. One could anticipate a significant increase in  $\Phi_{\beta\text{-cleavage}}$  if the ketone is placed in an environment that can limit conformational mobility and therefore reduce  $k_d$ . In the case of  $\beta$ -arylpropiophenones a similar effect on the phosphorescence can be achieved by inclusion of the ketones in certain zeolites<sup>27</sup> or cyclodextrins.<sup>28,29</sup>

Interestingly, we were unable to detect any products derived from benzyl radicals, which could be produced in the neophyl rearrangement of benzoylmethyl radicals.<sup>30</sup> For comparison, in the photodecomposition of  $\alpha$ -haloacetophenones neophyl products were detected in nonreactive solvents, such as benzene.<sup>3</sup> The likely explanation for this difference is probably in the formation of a very unreactive radical (phenoxyl) in reaction 1; under these conditions the slow<sup>30</sup> neophyl process cannot compete favorably with the scavenging by phenoxyl radicals whose steady-state concentration will be higher than that of alkyl or halogen radicals in the  $\alpha$ -haloacetophenone system.

Finally,  $\beta$ -cleavage processes similar to that illustrated in Scheme I and in reaction 5 may be involved in the photochemistry of lignins and ultimately in the yellowing of wood-derived products, especially paper. Interestingly, the effect of hydroxyl and methoxyl substituents as well as restricted mobility in the solid matrix may be important factors in determining the efficiency of the yellowing process. Studies designed to address these practical questions are currently in progress.

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