The Journal of Organic Chemistry

#### Article

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J. Org. Chem., Just Accepted Manuscript • DOI: 10.1021/acs.joc.0c01016 • Publication Date (Web): 04 Jun 2020 Downloaded from pubs.acs.org on June 6, 2020

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# Reactivity and Product Analysis of a Pair of Cumyloxyl and *tert*-Butoxyl Radicals Generated in Photolysis of *tert*-Butyl Cumyl Peroxide

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# **ABSTRACT:**



Alkoxyl radicals play important roles in various fields of chemistry. Understanding their reactivity is essential to applying their chemistry for industrial and biological purposes. Hydrogen atom transfer and C–C  $\beta$  scission reactions have been reported from alkoxyl radicals. The ratios of these two

processes were investigated using the cumyloxyl (CumO•) and *tert*-butoxyl radicals (*t*-BuO•), respectively. However, the products generated from the pair of radicals have not been investigated in detail. In this study, CumO• and *t*-BuO• were simultaneously generated from the photolysis of *tert*-butyl cumyl peroxide to understand the chemical behavior of the pair of radicals by analyzing the products and their distribution. Electron paramagnetic resonance and/or transient absorption spectroscopy analyses of radicals, including CumO• and *t*-BuO•, provide more information about the radicals generated during the photolysis of *tert*-butyl cumyl peroxide. Furthermore, the photoproducts of (3-(*tert*-butylperoxy)pentane-3-yl)benzene demonstrated that the ether products were formed in incage reactions. The triplet-sensitized reaction induced by acetophenone, which is produced from CumO•, clarified that the spin-state did not affect the product distribution.

## INTRODUCTION

Alkoxyl radicals play crucial roles in various fields of chemistry, such as autoxidation in chemical industry<sup>1</sup> and DNA damage caused by intracellular lipid peroxidation<sup>2,3</sup>. Alkoxyl radicals can be generated through thermal decomposition<sup>4</sup> and the Fenton reaction<sup>5</sup> of peroxides. The photochemical generation of alkoxyl radicals from di*-tert*-butyl peroxide ( $\mathbf{I}$ )<sup>6</sup> has been frequently used in the initiation of radical reactions for organic synthesis. In addition, pyridinethione ( $\mathbf{II}$ )<sup>7</sup>, pyridone ( $\mathbf{III}$ )<sup>8</sup>, perbenzoate ( $\mathbf{IV}$ )<sup>9</sup>, and thiazolethione ( $\mathbf{V}$ )<sup>10</sup> are known as radical donors in photolysis (Figure 1).



Figure 1. Precursors of alkoxyl radicals in photolysis

In the 1960s, Walling *et al.* reported the reactivity of alkoxyl radicals and clarified that the hydrogen atom transfer (HAT) and C–C  $\beta$ -scission reactions occur competitively (Figure 2)<sup>11</sup>. The ratios of these two processes were investigated using the cumyloxyl radical (CumO•, R = Ph) and the *tert*-butoxyl radical (*t*-BuO•, R = Me).<sup>12,13</sup> The ratio was found to be dependent on the solvent polarity, acidity, and steric effect. The reactivity of the two processes was discussed by Yurtsever *et al.* using quantum chemistry calculations,<sup>14</sup> indicating that the most stable products from CumO• and *t*-BuO• are VI and VII, respectively (Figure 3).



Figure 2. Reactivity of alkoxy radicals in hydrogen atom transfer (HAT) and C–C  $\beta$ -scission



Figure 3. Products with maximum stabilities that were obtained from CumO• and t-BuO•

There are few reports on the direct observation of the two alkoxyl radicals (CumO• and *t*-BuO•)<sup>15</sup> and the investigation of reaction products<sup>12a,16</sup>. The products of the alkoxy radicals have not been clarified in detail. In this study, we are interested not only in the products of alkoxy radicals but also in the products derived from the pair of radicals. The products derived from the radical pair cannot be distinguished in the photolysis of symmetrically substituted peroxides such as di-*tert*-butyl peroxide. To this end, in this study, the asymmetrically substituted *tert*-butyl cumyl peroxide derivatives **1a** and **b** were selected to determine the products derived from two alkoxyl radicals and the pair of radicals (Figure 4).



Figure 4. Photochemical decomposition of *tert*-butyl cumyl peroxide derivatives (1a,b) used in this

study.

#### **RESULTS AND DISCUSSION**

**Product analysis in the photolysis of 1a.** First, a UV-vis absorption spectroscopic analysis was conducted for the synthesized compound **1a** ( $\mathbf{R} = \mathbf{Me}$ ) (Figure 5). Structured absorption bands were observed at approximately 240–270 nm in acetonitrile. A 266 nm laser was chosen as the light source for the photoreaction of **1a**. The photoreaction of **1a** (20.5 mM) was conducted using a 266 nm laser (1 mJ/pulse, 10 Hz) in CD<sub>3</sub>CN (0.5 mL) at 25 °C under air or O<sub>2</sub> conditions (Table 1).



Figure 5. UV-vis absorption spectrum of 1a in acetonitrile.

After 1 h of photolysis in the nuclear magnetic resonance (NMR) tube, 11 photoproducts 2-11,11-d were detected and identified by <sup>1</sup>H NMR analysis (Table 1). The photoproducts were derived from the A, B, and A/B sides. The A-side products consisted of acetophenone (2),  $\alpha$ -cumyl alcohol

(3), and methyl cumyl ether (4). Acetone (5), *tert*-butanol (6), and *tert*-butyl methyl ether (7) were derived from the B-side products. Methanol (8), formaldehyde (9), ethane (10), methane (11), and mono-deuterated methane; CH<sub>3</sub>D (11-*d*) were found to be formed from the •CH<sub>3</sub> generated from the  $\beta$ -scission of the two alkoxy radicals. The chemical yields of the photoproducts and the conversion of 1a were determined using triphenylmethane as an internal standard (Table 1). The conversions of 1a under air and O<sub>2</sub> conditions was 70.8% and 72.2%, respectively (entries 1 and 2). Under air conditions ([O<sub>2</sub>] = 1.9 mM, entry 1), acetophenone (2) was exclusively formed in 94.1% of the A-side products, together with a small amount of alcohol 3 and ether 4. The selective formation of acetone (5) was found in 57.7% of the B-side products, together with a significant amount of the corresponding alcohol 6 (18.7%) and ether 7 (17.7%). The products 8-11 and 11-d derived from •CH<sub>3</sub> were identified by comparing the NMR signals of the authentic samples (Figure S2a-d). The oxygenated compounds 8 and 9 were derived from the reaction of the methyl radical with molecular oxygen.

Under O<sub>2</sub> conditions ([O<sub>2</sub>] = 9.1 mM, entry 2), an increase in the chemical yields of alcohols **3** and **6** and oxygenated compounds **8** and **9** were observed with the decrease in the formation of ethane (**10**) and ethers **4** and **7**, indicating that •CH<sub>3</sub> generated from β-scission from the alkoxy radicals escaped to the out-of-cage space to be trapped by O<sub>2</sub> to yield oxygenated compounds **8** and **9**. The decrease in the formation of ethers **4** and **7** also supports this mechanism. The reaction of •CH<sub>3</sub> with O<sub>2</sub> was computed at UB3LYP<sup>17</sup>/6-31G(d)<sup>18</sup> to be exothermic in the formation of methyl peroxide,  $\Delta H_{298} = -31.25$  kcal mol<sup>-1</sup>, without an energy barrier (Figure 6, Figure S35). The peroxide is the precursor for methanol (**8**)

and formaldehyde (**9**).  $^{19, 20}$ 



Table 1. Products and chemical yields in photolysis of 1a at 266 nm irradiation<sup>a</sup>

<sup>*a*</sup>Chemical yields of the photoproducts were calculated using triphenylmethane as an internal standard. Experimental error (%) is photoproduct chemical yield (%) x ( $\pm$  5-8%). <sup>*b*</sup>Triplet-sensitized photoreaction of **1a** (30 mM, Abs at 266 nm = 2.6) in the presence of acetophenone (**2**) (51mM, Abs at 266 nm = 34.7).



Figure 6. Generation and reactivity of •CH<sub>3</sub>

**Detection of alkoxyl radicals, CumO•, and t-BuO•**. In the product analysis mentioned above, two types of alkoxyl radicals, CumO• and *t*-BuO•, were proposed to be formed in the photolysis of **1a**. The detection of the two alkoxyl radicals was conducted by laser-flash-photolysis (LFP) and electron paramagnetic resonance (EPR) measurements. In the LFP measurements, 266 nm of light (Nd-YAG, 10 mJ/pulse, 10 ns pulse-width) was irradiated into the solution of **1a** (8.5 mM, MeCN, Abs = 1.1 at 266 nm) under air conditions at ~20 °C. After laser irradiation, the generation and decay of CumO• were detected at 485 nm<sup>15</sup> ( $k_{decay} = 6.7 \times 10^5$  s<sup>-1</sup>, Figure 7), which is consistent with the reported value of CumO•.<sup>15</sup>



Figure 7. Decay process of CumO• observed at 485 nm in the laser flash photolysis of 1a.

In the EPR measurements, the spin-trapping method was used to analyze the short-lived radicals. A solution of 1a and ~10 equivalents of the spin trapping reagent 5,5-dimethyl-1-pyrroline N-oxide (DMPO) (1a: 12 mM, DMPO: 141 mM, MeCN) was prepared. After photoirradiation of the solution in a flat quartz cell with a high-pressure Hg lamp under air at 25 °C, the typical EPR signals for nitroxides (R<sub>2</sub>N–O•) were detected (Figure 8a, Figure S19). To obtain information on the nitroxide structures, the spectra were compared with those observed in the photolysis of di-tert-butyl peroxide and dicumyl peroxide in the presence of DMPO (Figure 8b,c, Figures S20,21). The EPR signals obtained in the photolysis of 1a are consistent with the sum of the two EPR spectra obtained in the photolysis of the two peroxides. Futhermore, the simulated spectrum of the two nitroxides derived from the reaction of CumO• and t-BuO• with DMPO (nitroxides 12 and 13) was consistent with the experimentally observed spectrum, which can be seen by comparing Figure 8a with 8d. The triplet signals at g-values of 1.997, 2.006, and 2.015 with a hyperfine constant of 15.2 G were consistent with those obtained in the photolysis of DMPO in the absence of peroxides (Figure 8e, Figure S22). MS analysis of the product confirmed that the nitroxide signals were derived from 5,5-dimethylpyrrolidin-2-one oxide (Figure S34).





**Figure 8.** EPR spectra obtained after photolysis of **1a** and DMPO. (a) DMPO and di-*tert*-butyl peroxide, (b) DMPO and dicumyl peroxide, (c) simulation spectrum of sum of (b;  $a_N = 13.50$  G,  $a^{\beta}_H = 10.75$  G,  $a^{\gamma}_H = 1.27$  G), and (c;  $a_N = 13.42$  G,  $a^{\beta}_H = 11.05$  G,  $a^{\gamma}_H = 1.28$  G) (not included **\*** peaks), and (d) spectrum obtained after photoirradiation of DMPO (e)

To obtain information about the structures detected in the photoreaction of **1a** and DMPO, an MS analysis was conducted on the photolysate (Figure 9, Figures S29-32). In addition to the mass numbers of the two alkoxyl-radical-trapped nitroxides **12** (MS 180.15) and **13** (MS 248.17), three radical trapping compounds **14–16** were detected, indicating that methyl, methoxyl, and hydroxyl radicals were formed during the photolysis of **1a**.



Figure 9. Five spin adducts were detected by electrospray ionization-MS (FTMS, Positive) measurements.

**Mechanism.** The mechanism of the photochemical reaction of **1a** ( $\mathbf{R} = \mathbf{CH}_3$ ) is summarized in Scheme 1, which is proposed on the basis of the products and spectroscopic observations. After the homolytic O–O bond cleavage of **1a**, the radical pair of CumO• (**A**:  $\mathbf{R} = \mathbf{CH}_3$ ) and *t*-BuO• **B** is generated, which followed by the  $\beta$ -scission reaction that lead to the production of ketones **2** ( $\mathbf{R} = \mathbf{CH}_3$ ) and **5**, as well as •CH<sub>3</sub> and  $\mathbf{R}$ • ( $\mathbf{R} = \mathbf{CH}_3$ ). Moreover, HAT produces corresponding alcohols **3** ( $\mathbf{R} =$ CH<sub>3</sub>) and **6**. The released •CH<sub>3</sub> reacts with the alkoxyl radicals to produce ethers **4** ( $\mathbf{R} = \mathbf{CH}_3$ ) and **7**. Once the •CH<sub>3</sub> is trapped by O<sub>2</sub>, methanol (**8**) and formaldehyde (**9**) are formed after the O–O bond cleavage, from which methoxyl and hydroxyl radicals can be generated. The dimerization of •CH<sub>3</sub> produces ethane (**10**). Methane (**11**) can be formed by the hydrogen atom abstract from •CH<sub>3</sub>. The deuterated isomer is formed by deuterium-atom abstraction from CD<sub>3</sub>CN. As shown in Scheme 1, the mechanism of the formation of products in the photolysis of **1a** is reasonable based on the product and spectroscopic analyses.





There are some additional questions. The first question concerns the source of hydrogen atoms. As judged by the bond dissociation energies<sup>21</sup>, the C-H bond dissociation energy of acetonitrile is the lowest, indicating that the hydrogen sources are CH<sub>3</sub>CN, CDH<sub>2</sub>CN, and CD<sub>2</sub>HCN, which are contaminated in 99%-d CDCN<sub>3</sub>. In fact, deuterated methane (**11**-d, CH<sub>3</sub>D) was detected by an NMR 12

analysis of the photolysate (Figure S2d). Other hydrogen sources are **1a** and/or photoproducts such as acetophenone (**2**) because non-deuterated methane (**11**-d) was observed during photolysis.

The second question concerns the difference in the chemical yields of ketones 2 and 5, which are the products of the  $\beta$ -scission from CumO• and *t*-BuO•, respectively. Thus, the chemical yield of 2 (~90%) was significantly higher than that of 5 (~50%). This is because of the differences in the transition-state energies in the  $\beta$ -scissions of CumO• and *t*-BuO•. From the quantum chemical calculations at the UB3LYP<sup>17</sup>/6-31G(d)<sup>18</sup> level, the  $\beta$ -scission energy in CumO• was found to be lower than that of *t*-BuO• by ~2 kcal mol<sup>-1</sup> due to the stabilization effect of the phenyl ring (Figure 10). Indeed, the faster  $\beta$ -scission in CumO• than that in *t*-BuO• was experimentally found to be  $k_{\beta} = 7.4 \times 10^5 \text{ s}^{-1}$  and 6.4 ×  $10^5 \text{ s}^{-1}$ , respectively.<sup>12b,13e</sup> The longer-lived *t*-BuO• has a greater chance to abstract a hydrogen atom and react with •CH<sub>3</sub> to yield an alcohol (6) and ether (7), respectively. The difference in the  $\beta$  scission energy between CumO• and *t*-BuO• is key to understanding the product distribution.



**Figure 10.** Difference in the  $\beta$ -scission transition energy between A side (CumO•) and B side (*t*-BuO•). The energies were calculated at the UB3LYP/6-31G(d) level of theory.

The third question is whether ether products **4** and **7** are in-cage or out-of-cage products. Because both alkoxyl radicals can release •CH<sub>3</sub>, it is difficult to distinguish the two processes. To solve this problem, (3-(*tert*-butylperoxy)pentane-3yl)benzene (**1b**), in which the methyl substituents are replaced by ethyl substituents, was synthesized from 1-ethyl-1-phenylpropyl hydroperoxide (see the experimental section) and was irradiated under similar conditions as **1a** (Figure 11).



Figure 11. Photoreaction of (3-(*tert*-butylperoxy)pentane-3yl)benzene (1b)

The alkoxyl radicals 1-ethyl-1-phenylpropoxyl (EPPO•) and *tert*-butoxyl (*t*-BuO•), are generated during the photolysis of **1b**, followed by  $\beta$ -scission reactions to produce •C<sub>2</sub>H<sub>5</sub> and •CH<sub>3</sub>. It is possible to understand the reaction pathway for in-cage reactions and/or out-of-cage reactions, which produce ether products. The UV-vis absorption spectrum of **1b** (Figure S15) is very similar to that of **1a**. The photoreaction of **1b** was also conducted using a 266 nm laser as a light source. After the photoreaction of **1b** (20.2 mM, in CD<sub>3</sub>CN) under air at 25 °C for 1 h, the photoproducts **5-11**, **17**, and **21-26** were detected by <sup>1</sup>H NMR analysis (Table 2, Figure S4a-e). The chemical yields of the photoproducts and the conversion yields of the photoreaction were calculated using triphenylmethane as an internal standard for the photolysis of **1a** (Table 2).

# Table 2. Products and chemical yields during photolysis of 1b at 266 nm irradiation<sup>a</sup>



"Chemical yields of photoproducts were calculated using triphenylmethane as internal standard. Experimental error (%) is photoproduct chemical yield (%) × ( $\pm$  5-8%). <sup>b</sup>The chemical yields of 23, 10-*d*, and 26 were not calculated due to overlap of these <sup>1</sup>H NMR peaks.

Interestingly, alcohol and ether products **18–20** were not detected in the A-side products derived from EPPO• (**A**: **R** = CH<sub>2</sub>CH<sub>3</sub>, Scheme 1). To understand the effect of the ethyl group on the product selectivity, the transition-state structure of the  $\beta$ -scission process was computed at the same level of theory (Figure 12). The Gibbs activation energy of the  $\beta$ -scission process in EPPO• was found to be  $\Delta G_{298}^{\ddagger} = 7.24$  kcal/mol, which was lower than those in CumO• and *t*-BuO• by ~4 kcal mol<sup>-1</sup> and ~6 kcal mol<sup>-1</sup>, respectively. Bietti *et al.* reported that the C–Et  $\beta$ -scission in 2-(4-methylphenyl)-2-butoxyl





**Figure 12.** Difference in the  $\beta$ -scission transition energy between the A side (EPPO•) and the B side (*t*-BuO•). Energies were calculated at UB3LYP/6-31G(d) level of theory.

It should be noted that *tert*-butyl ethyl ether (**25**) was more preferentially formed than *tert*-butyl methyl ether (**7**). This observation can be explained by the in-cage reaction of the pair of radicals EPPO• and *t*-BuO•. Thus,  $\bullet$ C<sub>2</sub>H<sub>5</sub> is released rapidly from EPPO• at the A-side owing to the fast  $\beta$ -scission process. Another radical in the radical pair, *t*-BuO•, has a greater opportunity to react with  $\bullet$ C<sub>2</sub>H<sub>5</sub> to yield ether

**25** than the reaction with •CH<sub>3</sub> (Figure 13a), which is released from the  $\beta$ -scission reaction of *t*-BuO• (Figure 13b). These results suggest that the ethers at the B side in the photolysis of **1a** are mainly generated from in-cage reactions (Scheme 1).



Figure 13. (a) In-cage reaction (b) Out-of-cage reaction

Importantly, ethylene (24) was detected during the photolysis of 1b (Figure S4c). The formation of ethylene (24) was derived from the in-cage reaction of  $\cdot$ C<sub>2</sub>H<sub>5</sub>, which is generated from the  $\beta$ -scission of EPPO $\cdot$ , with *t*-BuO $\cdot$  (Figure 14) because the chemical yield of *tert*-butanol (6) in the photolysis of 1b was higher than that in the photolysis of 1a. The mechanism of the photochemical decomposition of 1b (R = CH<sub>2</sub>CH<sub>3</sub>) is also summarized in Scheme 1. The alkoxyl radical A (R = CH<sub>2</sub>CH<sub>3</sub>) at the A

side releases more R• than •CH<sub>3</sub> from the B side because the  $\beta$ -scission transition-state energy at the A side is lower than that of the B side. The lifetime of alkoxyl radical **A** (R = CH<sub>2</sub>CH<sub>3</sub>) is shorter than that of *t*-BuO• (= **B**). The relatively high chemical yields of ethane (**10**) even under oxygen atmosphere can also be explained by the in-cage reaction (Scheme 1). Thus, the methyl radicals generated by the  $\beta$ -scission from CumO• and *t*-BuO• are coupled each other to give ethane before reacting with molecular oxygen, although the oxygenation process is supposed to be barrierless (Figure 6).



Figure 14. Formation of *tert*-butanol (6) and ethylene (24)

Effects of acetophenone on product distribution. When the photoreaction of **1a** (3.7 mM in MeCN) using a 266 nm laser was monitored by a UV-vis spectrometer, the absorption spectrum of **1a** (blue line in Figure 15) gradually changed to the red spectrum after 1 h of irradiation. The red spectrum is consistent with the spectrum of acetophenone (**2**), indicating that the 266 nm light mainly excites **2** after 30 min of the photolysis of **1a**. The product distribution of the acetophenone-induced decomposition of **1a** should be investigated to understand the mechanism.



Figure 15. Time-dependent change in the absorption spectrum during the photoreaction of 1a (3.7 mM, MeCN) using a 266 nm laser (1 mJ) under air at 25 °C. UV-vis absorption spectrum of acetophenone (2) in MeCN.

First, the rate of the photochemical decomposition of 1a was analyzed to determine whether acetophenone affects the decomposition efficiency of 1a (Figure 16). A solution of 1a (24.9 mM) and benzene (99.9 mM) in CD<sub>3</sub>CN was irradiated with a 266 nm laser (1 mJ) for 7 h under air at room temperature (~22 °C). By comparing the integration of the benzene signal with that of **1a** on the <sup>1</sup>H NMR spectra, the rate of decomposition of 1a was determined. As shown in Figure 16a, the decomposition of **1a**, that is, the conversion (%), was monoexponentially increased to 100 % during photolysis at 266 nm, suggesting that the decomposition rate induced by the acetophenone triplet is similar to that of the direct decomposition of **1a**. When the chemical yields of the six photoproducts **2**, 5, 6, 7, 11, and 11-d were plotted against the irradiation time, mono-exponential increases of these





Figure 16. (a) Photoreaction conversion yield of 1a, (b) change in the amount of 1a and photoproducts

(2, 5, 6, 7, 11, and 11-*d*) (mmol) with photoirradiation time.

The mechanism of the acetophenone-induced decomposition is the energy transfer from the triplet acetophenone to **1a**, because the triplet energy of acetophenone, at 66.2 kcal mol<sup>-1</sup>, is higher than that of the triplet state of **1a**, 24.0 kcal mol<sup>-1</sup>, which was computed at the B3LYP/6-31G(d) level of theory. The quenching reaction of acetophenone by **1a** was confirmed by LFP experiments (266 nm, Nd-YAG, 6-7 mJ/pulse, 10 ns pulse-width, Eq. 1, Figure 17). The triplet acetophenone at 320 nm, which is the triplet-triplet absorption maximum (Figure 17a)<sup>22</sup>, was quenched by **1a** with a quenching rate constant of **1a**;  $k_q = 1.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$  (Figure 17b). The weak negative signal at ~420 nm is derived from the phosphorescence of <sup>3</sup>**2**\*,<sup>22b</sup> because the decay rate constant,  $k_d = 1.0 \times 10^6 \text{ s}^{-1}$ , was consistent with the rise signal at 420 nm. The alkoxyl radical CumO• at 485 nm in the triplet-sensitized photolysis of **1a** was also detected under air, N<sub>2</sub>, and O<sub>2</sub> conditions at room temperature (~23 °C) (Figure 17c).

 $2 \xrightarrow{h\nu} {}^{3}2^{*} \xrightarrow{k_{q}} {}^{3}[1a]^{*} \cdots (1)$ 



**Figure 17.** (a) Transient absorption spectrum of acetophenone (2) (1.7 mM, Abs at 266 nm = 1.1) at 25 °C under N<sub>2</sub>. (b) Decay process of acetophenone triplet with/without **1a**, which was monitored at 320 nm at room temperature under N<sub>2</sub>; (c) Decay process of CumO• generated during photolysis of

**1a** (11.2 mM, Abs at 266 nm = 0.9) in the presence of large amount of acetophenone (**2**) (5.6 mM, Abs at 266 nm = 3.8) under air, N<sub>2</sub>, and O<sub>2</sub> conditions, which were monitored at 485 nm.

The product distribution of the acetophenone-triplet-induced decomposition of **1a** was examined in the presence of a significant excess of **2** (entry 3 in Table 1). The absorbance of acetophenone at 266 nm was 14 times higher than that of **1a**. After the 266 nm laser irradiation of this mixture for 2 h, the product distribution was roughly the same as that observed in the photolysis of **1a**. This result suggests that the photoproduct distribution of **1a** is not dependent on the spin state or the singlet/triplet, whose phenomena are consistent with those observed in Figure 16.

#### CONCLUSIONS

In the present study, the reactivity and chemical fate of the pair of radicals, CumO• and *t*-BuO• which were simultaneously generated, were investigated in detail in the photolysis of **1a** ( $\mathbf{R} = CH_3$ ). The photoproducts and their distributions were carefully analyzed by <sup>1</sup>H NMR spectroscopy. The alkoxyl radicals produced the corresponding ketones, alcohols, ethers, methane, ethane, methanol, and formaldehyde in the photolysis of **1a**. The product ratio was largely dependent on the substituents. Thus, the chemical yield of acetophenone (**2**) from CumO• was much higher than that of acetone (**5**) from *t*-BuO• because the β-elimination reaction in CumO• is faster than that in *t*-BuO•. Primarily ether product **7** was found to be formed in the pair of radicals, which was an in-cage reaction because ether

**25** preferentially formed over **7** in the photolysis of **1b** ( $\mathbf{R} = CH_2CH_3$ ). From the laser flash photolysis, EPR measurements, and MS analyses, the generation of the two types of alkoxyl radial intermediates as well as the generation of radicals from the alkoxy radicals were confirmed in the photolysis of **1a**. The energy transfer from the triplet acetophenone (**2**) to **1a** was also confirmed by analyzing the fall process of triplet acetophenone in the presence of **1a**, indicating that the photoproduct distribution of **1a** is independent of the spin state of the excited state of **1a**.

# **EXPERIMENTAL SECTION**

General Information. Materials obtained from commercial suppliers were used as received. Otherwise noted, all reactions were performed with dry solvents under an atmosphere of nitrogen gas in dried glassware. All workup and purification procedures were carried out with reagent grade solvents in air. Thin-layer chromatography (TLC) analyses were performed on commercial aluminium sheets of Merck silica gel 60F254 and visualized with ultraviolet lamp ( $\lambda = 254$  nm). Purification was done by column chromatography using silica gel (63-210 µm). NMR spectra were recorded on a Bruker Ascend 400 to give <sup>1</sup>H NMR (400 MHz) spectra and <sup>13</sup>C NMR (100 MHz) spectra. Chemical shifts for <sup>1</sup>H NMR are expressed in parts per million (ppm) relative to tetramethylsilane ( $\delta$  0.00 ppm) or the residual peak of CDCl<sub>3</sub> ( $\delta$  7.26 ppm) or CD<sub>3</sub>CN ( $\delta$  1.94 ppm). Chemical shifts for <sup>13</sup>C NMR are expressed in ppm relative to CDCl<sub>3</sub> ( $\delta$  77.16 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, dq = doublet of

> quartets, br = broad signal, m = multiplet), coupling constant (Hz), and integration. UV-vis spectra were recorded on a SIMADZU UV-3600 Plus spectrophotometer. Gas chromatography-mass spectra (GC-HRMS) were conducted on an Agilent 7890A GC system equipped with a HP-5 column (0.32 mm × 0.25  $\mu$ m × 30 m; Split ratio 10 : 1, inject temperature: 200°C, column temperature program: 50°C, 10°C min<sup>-1</sup> to 300°C) using Field ionization positive (FI+; 10 kV) for separating compound **1**, methyl 1-ethyl-1-phenylpropyl ether and ethyl 1-ethyl-1-phenylpropyl ether. High-resolution mass spectra (HRMS) were performed with a Thermo Fisher Scientific LTQ Orbitrap XL using electrospray ionization (ESI) method. EPR spectra were recorded on a Bruker BioSpin Elexsys E500.

# Synthesis

*tert-Butyl Cumyl Peroxide (1a):* The compound was prepared according to a known procedure<sup>23</sup>. Added a stirring bar to the two-necked flask, drew a vacuum with drying, and purged with nitrogen. Trichloroacetimidate (0.21 mL, 1.17 mmol) and a solution of cumene hydroperoxide (119.5 mg, 0.79 mmol) in CH<sub>2</sub>Cl<sub>2</sub> 1 mL were added to the flask, and the flask was cooled to  $-20^{\circ}$ C (NaCl + ice water ) with stirring. Then BF<sub>3</sub>-Et<sub>2</sub>O diluted with CH<sub>2</sub>Cl<sub>2</sub> (0.6 mL, 0.03 mmol) was dropped slowly to the reaction mixture. When the reaction temperature reached to room temperature, a small amount of NaHCO<sub>3</sub> was added to the reaction mixture for quenching, and solid was removed by filtration. After evaporating and purification with column chromatography (hexane/CH<sub>2</sub>Cl<sub>2</sub> = 20 : 1, R<sub>f</sub> = 0.28), **1a** (51 mg, 0.24 mmol, 19%) was obtained as colorless oil. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  (ppm) 7.12

(d, J = 7.1 Hz, 2H), 7.24 (dd, J = 7.5, 7.5 Hz, 2H), 7.24 (t, J = 7.3 Hz, 1H), 1.53 (s, 6H), 1.21 (s, 9H). UV-vis (CH<sub>3</sub>CN, c = 5.5 mM):  $\lambda_{max}$  ( $\varepsilon$ ) = 257 (178) nm (M<sup>-1</sup> cm<sup>-1</sup>). The spectroscopic data are consistent with those reported in the literature<sup>24</sup>. *Methyl cumyl ether (4):* The compound was prepared according to a known procedure<sup>25</sup>. NaH (60 wt% oil dispersion) (0.683 g, 17.1 mmol) was added to a two necked-flask and the flask was purged with nitrogen. Then, THF (10 mL) was added to the flask and stirred over 30 min. To the mixture was  $\alpha$ -cumyl alcohol dissolved in THF (3 mL) was added, and then stirred over 30 min. Finally, CH<sub>3</sub>I was added to the reaction mixture and stirred overnight. After finished the reaction, H<sub>2</sub>O (15 mL) was

with those reported in the literature<sup>25</sup>.

with nitrogen. Then, THF (10 mL) was added to the flask and stirred over 30 min. To the mixture was  $\alpha$ -cumyl alcohol dissolved in THF (3 mL) was added, and then stirred over 30 min. Finally, CH<sub>3</sub>I was added to the reaction mixture and stirred overnight. After finished the reaction, H<sub>2</sub>O (15 mL) was added, and then the mixture was extracted with EtOAc. The organic layer was dried over MgSO<sub>4</sub>, concentrated, and purified via silica gel column chromatography (hexane/EtOAc = 5 : 1, R<sub>f</sub> = 0.55) to obtain **4** (569 mg, 3.8 mmol, 79%) as colorless oil. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  (ppm) 7.42 (d, *J* = 7.1 Hz, 2H), 7.35 (dd, *J* = 7.6, 6.8 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 3.00 (s, 3H), 1.47 (s, 6H). UV-vis (CH<sub>3</sub>CN, c = 6.3 mM):  $\lambda_{max}$  ( $\varepsilon$ ) = 257 (183) nm (M<sup>-1</sup> cm<sup>-1</sup>). The spectroscopic data are consistent

*1-Ethyl-1-phenylpropanol (18):* The compound was prepared according to a known procedure<sup>26</sup>. Methyl benzoate (1.36 g, 10 mmol) and dry THF (20 mL) were added to a two-necked flask. Under N<sub>2</sub> atmosphere, the solution was cooled to 0°C followed by drop-wise addition of EtMgBr (in THF, abt. 1 M) (30 mL, 30 mmol). The mixture was stirred at room temperature overnight. The reaction mixture was diluted with EtOAc and then, saturated aqueous NH<sub>4</sub>Cl was added. The organic phase

was extracted with EtOAc, washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The product was purified by silica column chromatography (hexane/EtOAc = 50 : 1,  $R_f = 0.13$ ) to afford **18** (1.44 g, 8.78 mmol, 88%). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  (ppm) 7.38 (d, J = 7.2 Hz, 2H), 7.32 (dd, J = 7.7, 7.7 Hz, 2H), 7.20 (t, J = 7.9 Hz, 1H), 2.71 (br, 1H), 1.81 (dq, J = 14.4, 7.5 Hz, 2H), 1.74 (dq, J = 14.1, 7.3 Hz, 2H), 0.67 (t, J = 7.4 Hz, 6H). The spectroscopic data are consistent with those reported in the literature<sup>26</sup>.

*1-Ethyl-1-phenylpropyl hydroperoxide:* The compound was prepared according to a known procedure<sup>27</sup>. A solution of 1-ethyl-1-phenylpropanol dissolved in methanol (5 mL) was added dropwise to the stirred mixture of 30% H<sub>2</sub>O<sub>2</sub> (150 mL) and 2.5% H<sub>2</sub>SO<sub>4</sub> (15 mL). After stirring for 5 h at room temperature, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with water, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The hydroperoxide product was given as colorless oil (purity : 88%, 324.6 mg, 1.58 mmol, 79%). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  (ppm) 8.72 (br, 1H), 7.38-7.32 (m, 4H), 7.27-7.23 (m, 1H), 1.87 (dq, *J* = 10.9, 6.7 Hz, 4H), 0.72 (t, *J* = 7.4 Hz, 6H). The spectroscopic data are consistent with those reported in the literature<sup>27</sup>.

(3-(tert-butylperoxy)pentane-3yl)benzene (1b): The compound was prepared according to a known procedure<sup>23</sup>. Added a stirring bar to the two-necked flask, drew a vacuum with drying, and purged with nitrogen. Trichloroacetimidate (0.24 mL, 1.34 mmol) and a solution of hydroperoxide, 1-ethyl-1-phenylpropyl (161.1 mg, 0.89 mmol) in CH<sub>2</sub>Cl<sub>2</sub> 1.3 mL were added to the flask, and the flask was cooled to -20°C (NaCl + ice water ) with stirring. Then BF<sub>3</sub>-Et<sub>2</sub>O diluted with CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL,

0.036 mmol) was dropped slowly to the reaction mixture. When the reaction temperature reached to room temperature, a small amount of NaHCO<sub>3</sub> was added to the reaction mixture for quenching, and solid was removed by filtration. After evaporating and purification with column chromatography (hexane,  $R_f = 0.50$ )<sup>28</sup>, **1b** was obtained as colorless oil (58.6 mg, 0.25 mmol, 32%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.34-7.28 (m, 4H), 7.23-7.18 (m, 1H), 2.02 (dq, J = 14.0, 7.4 Hz, 2H), 1.81 (dq, J = 14.0, 7.4 Hz, 2H), 1.28 (s, 9H), 0.71 (t, J = 7.4 Hz, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 143.6 (C), 127.6 (CH), 126.2 (CH), 126.1 (CH), 85.9 (C), 78.4 (C), 29.3 (CH<sub>2</sub>), 26.8 (CH<sub>3</sub>), 7.8 (CH<sub>3</sub>). HRMS (FI+) m/z: [M]<sup>+</sup> calcd for C<sub>15</sub>H<sub>24</sub>O<sub>2</sub> 236.1776<sup>3</sup>; found 236.1769<sup>5</sup>. UV-vis (CH<sub>3</sub>CN, c = 10.2 mM):  $\lambda_{max}$  (c) = 257 (196) nm (M<sup>-1</sup> cm<sup>-1</sup>).

*Methyl 1-ethyl-1-phenylpropyl ether (19):* The compound was prepared according to a known procedure<sup>25</sup>. NaH (60 wt% oil dispersion) (159.3 mg, 3.98 mmol) was added to a two necked-flask and the flask was purged with nitrogen. Then, THF (2.2 mL) was added to the flask and stirred over 30 min. To the mixture was alcohol compound (188.2 mg, 1.14 mmol) dissolved in THF (1 mL) was added, and then stirred over 30 min. Finally, CH<sub>3</sub>I (0.23 mL, 3.65 mmol) was added to the reaction mixture and stirred overnight. After finished the reaction, H<sub>2</sub>O (3.3 mL) was added, and then the mixture was extracted with EtOAc. The organic layer was dried over MgSO<sub>4</sub>, concentrated, and purified via silica gel column chromatography (hexane,  $R_f = 0.23$ ) to obtain **19** as colorless oil (199 mg, 1.12 mmol, 98%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.38-7.30 (m, 4H), 7.23 (t, *J* = 6.9 Hz, 1H), 3.06 (s, 3H), 1.88 (dq, *J* = 14.7, 7.5Hz, 2H), 1.82 (dq, *J* = 12.9, 7.4 Hz, 2H), 0.71 (t, *J* = 7.4 Hz).

6H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 144.3 (C), 127.9 (CH), 126.6 (CH), 126.5 (C), 81.5 (C), 49.4 (CH<sub>3</sub>), 28.1 (CH<sub>2</sub>), 7.5 (CH<sub>2</sub>). 0HRMS (FI+) *m/z*: [M]<sup>+</sup> calcd for C<sub>12</sub>H<sub>18</sub>O<sub>1</sub> 178.1357<del>6</del>; found 178.1362<del>3</del>.

Ethyl 1-ethyl-1-phenylpropyl ether (20): The compound was prepared according to a known procedure<sup>25</sup>. NaH (60 wt% oil dispersion) (151.7 mg, 0.92 mmol) was added to a two necked-flask and the flask was purged with nitrogen. Then, THF (1.7 mL) was added to the flask and stirred over 30 min. To the mixture was alcohol compound (151.7 mg, 0.92 mmol) dissolved in THF (1 mL) was added, and then stirred over 30 min. Finally, C<sub>2</sub>H<sub>5</sub>I (0.24 mL, 2.94 mmol) was added to the reaction mixture and stirred overnight. After finished the reaction,  $H_2O$  (2.6 mL) was added, and then the mixture was extracted with EtOAc. The organic layer was dried over MgSO<sub>4</sub>, concentrated, and purified via silica gel column chromatography (hexane,  $R_f = 0.11$ ) to get 20 as colorless oil (21.1 mg, 0.11 mmol, 12%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.39 (d, J = 7.1 Hz, 2H), 7.32 (dd, J = 7.7, 7.7 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 3.18 (q, J = 6.9 Hz, 2H), 1.89 (dq, J = 16.5, 7.4 Hz, 2H), 1.82 (dq, J = 16.3, 7.4 Hz, 2H), 1.18 (t, J = 7.0 Hz, 3H), 0.70 (t, J = 7.4 Hz, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, 100 MHz, 100 MHz) CDCl<sub>3</sub>):  $\delta$  (ppm) 144.9 (C), 127.8 (CH), 126.5 (CH), 126.3 (CH), 81.2 (C), 56.5 (CH<sub>2</sub>), 28.6 (CH<sub>2</sub>), 15.7 (CH<sub>3</sub>), 7.5 (CH<sub>3</sub>). HRMS (FI+) m/z: [M]<sup>+</sup> calcd for C<sub>13</sub>H<sub>20</sub>O<sub>1</sub> 192.15141; found 192.15127.

**Photoreaction.** The mother solution for all photoreactions was prepared using a volumetric flask and acetonitrile-d<sub>3</sub> (CD<sub>3</sub>CN, 99.9%D). 0.35 mL of the solution was added to 3-4 quartz tubes

using a syringe, respectively. When the sample solution was placed under oxygen conditions, oxygen bubbling was performed for 15 minutes. The photoreactions were conducted using Nd: YAG laser (LOTIS TII: LS-2145TF) which produces 10 Hz pulse of 1 mJ at 266 nm (beam diameter: 3 cm using a beam expander lens) as light source. The photoproducts were directly analyzed by <sup>1</sup>H NMR spectroscopy. The chemical yields of photoproducts were calculated using triphenylmethane as an internal standard. The experimental error was calculated from the results of 3-4 times photoreactions.<sup>29</sup>

UV-Vis Absorption Spectroscopy. All samples were measured in acetonitrile (MeCN, Spectro grade) and 10 mm  $\times$  10 mm quartz cell.

**EPR Spin-Trapping Experiments.** All procedures were conducted under dark conditions due to the photosensitivity of 5,5-Dimethyl-1-pyrroline N-Oxide (DMPO). The sample solution was prepared using volumetric flask and acetonitrile (MeCN, Spectro grade). An aqueous flat cell was used for measuring EPR spectra of the photoreaction sample. All photoreaction measurements were performed at room temperature (~25°C) using a high-pressure Hg lamp (Hamamatsu Photonics, LIGHTNINGCURE: L9566) without filter for generating a lot of radicals at the same time. The main emitted wavelengths are 254, 313, 365, 407, 440, and 550 nm. EPR spectra were obtained at modulation frequency: 100 kHz, smooth point: 1, number of scan: 3, modulation amplitude: 0.3 G, receiver gain: 60 dB, number of points: 16384, and sweep time: 81.92 ms.

Laser-Flash-Photolysis Measurements. All samples were detected at room temperature (20-23°C) by Laser Flash Photolysis (LFP), using a LOTIS TII: LS-2145TF Nd: YAG laser (266 nm, ca.

7-10 mJ/pulse, 10 ns pulse-width). The monitoring system consisted of a 150 W xenon lamp as a light source, Unisoku-MD200 monochromator and a photomultiplier. The sample solution was prepared using MeCN (Spectro grade) and Abs was adjusted to  $0.5 \sim 1.0$ . A 5 mm (in the direction of the laser beam)  $\times$  10 mm (in the direction of the analyzing light) quartz cell was used for LFP measurements. The fall process of CumO• was detected at 485 nm under air, N<sub>2</sub> and O<sub>2</sub> conditions. The fall process of acetophenone-triplet was detected at 320 nm under N<sub>2</sub> condition.

**DFT Calculations.** DFT calculations were carried out using the Gaussian 09 programming package<sup>30</sup>. All results were obtained with B3LYP<sup>17</sup>/6-31G (d)<sup>18</sup> level of theory in Gas Phase.

#### ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website.

Figures of NMR spectra, UV-vis absorption spectra, 2D TLC analysis, EPR spectra, Mass spectra,

data of DFT calculations (PDF)

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#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENT

M.A. greatly acknowledges financial support by JSPS KAKENHI (grant no, JP17H03022). We thank N-BARD, Hiroshima University, for EPR and MS measurements.

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