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Production and Excited State Dynamics of the Photorearranged Isomer of Benzyl Chloride and Its Methyl Derivatives Studied by Stepwise Two-Color Laser Excitation Transient Absorption and Time-Resolved Thermal Lensing Techniques

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Production and photoexcited dynamics of reaction intermediates with photolyses of benzyl chloride (BzCl) and methyl-substituted benzyl chlorides (MeBzCls) were studied by using stepwise two-color laser excitation transient absorption (TC-TA) and two-color laser excitation time-resolved thermal lensing (TC-TRTL) measurements. With photoexcitation of BzCl the formation of transient photorearranged isomer was suggested in the previous paper [*Res. Chem. Intermed.* **2001**, *27*, 137]. Such an isomer formation for MeBzCls was also observed in a 248 nm excitation. It was found that further photoexcitation of the isomers with the 308 nm light caused photodissociation to yield the corresponding benzyl radicals. The reaction quantum yield and the molar absorptivity of the photorearranged isomer of BzCl were estimated. The heat of reaction for the photodissociation of the isomer was successfully determined with the TC-TRTL measurement. These experimental results were consistent with MO calculations.

Introduction

Benzyl radical (Bz) is one of the most basic aromatic free radicals and is of importance in many chemical reactions. A large number of spectroscopic investigations for Bz and its derivatives have been reported since the 1950s in rigid glasses or films at low temperature,[1,2] in gas phase,[3−5] in supersonic jet expansion,[6−8] and in liquid phase.[9−12] Reaction and relaxation dynamics from their vibrationally or electronically excited states also have been studied in recent years.[13−18] Benzyl chlorides (BzCls) have been frequently used as a radical source because photoexcitation of BzCl induces the carbon−chlorine bond homolysis to generate Bz and a chlorine atom (Cl) with high quantum yield.[12,19−23]

Upon photolysis of BzCl, a quite long-lived transient, which has a broad absorption band at around 320 nm, was observed in oxygen-free *n*-hexane in addition to Bz. Tokumura et al. assigned it to the benzyl cation.[10] Recently Hiratsuka et al.[24] suggested that the transient should be a structural isomer of BzCl produced by the recombination of Bz and Cl atoms in a solvent cage, analogous to the photolyses for phenylacetate[25] and trimethylsilyldiphenylmethane.[26] We recently investigated the reaction intermediate produced by the photolysis of 2-(bromomethyl)naphthalene in hexane solution using one-color and stepwise two-color laser excitation transient absorption methods and ab initio calculations.[27] In addition to formation of the 2-naphthylmethyl radical, a long-lived transient species, which is supposed to be a photorearranged isomer of 2-(bromomethyl)-naphthalene, was observed after the photoexcitation. It was also found that further excitation of the long-lived transient species should result in photodissociation to yield the 2-naphthylmethyl radical.

In recent years, a time-resolved thermal lensing (TRTL) method has been used as one of the most sensitive techniques to directly detect the heat released through nonradiative processes of excited molecules.[28,29] Especially, the technique is powerful for the investigation of nonfluorescent species. The high sensitivity of the method enables us to measure the species at low concentration. Therefore, the two-color laser excitation TRTL (TC-TRTL) technique gives us information on dynamics of transient molecules in the excited state, which is unobtainable by fluorescence and transient absorption measurements.[30−33]

In this article, production and excited-state dynamics of the photorearranged isomers of BzCl and the *o*-, *m*-, and *p*-methylbenzyl chlorides (*o*-, *m*-, and *p*-MeBzCls) were studied with one-color and stepwise two-color laser excitation transient absorption (TC-TA) and TC-TRTL measurements. The combination of the two-color excitation techniques gives us dynamical and calorimetric information on the excited isomers. Ab initio and density functional theory (DFT) calculations were also carried out to obtain information on the conformation and the electronic structure of the isomers.

Experimental Section

Materials. Benzyl chloride (BzCl) (α-chlorotoluene; Tokyo Kasei Indus.; GR grade) was purified by distillation. 1,3-Diphenyl-2-propanone (dibenzyl ketone; EP grade), *o*-methylbenzyl chloride (*o*-MeBzCl) (α-chloro-*o*-xylene; GR grade), *m*-methylbenzyl chloride (*m*-MeBzCl) (α-chloro-*m*-xylene; EP grade), and *p*-methylbenzyl chloride (*p*-MeBzCl) (α-chloro-*p*-xylene; EP grade) were purchased from Tokyo Kasei Indus.,

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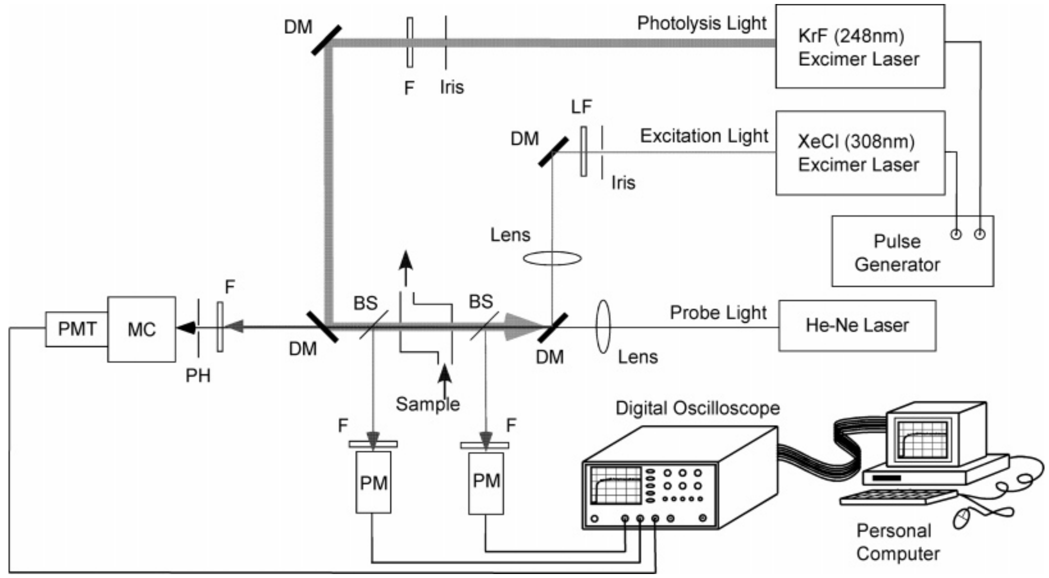

Figure 1. Experimental setup for the TC-TRTL measurement: MC, monochromator; PMT, photomultiplier tube; BS, beam splitter; LF, linear-wedge filter; PH, pinhole; F, filter; DM, dichroic mirror; PM, power meter.

and were used from a freshly opened bottle. 2-Hydroxybenzophenone (2-benzoylphenol; Tokyo Kasei Indus.; EP grade) was purified by recrystallization in methanol. Hexane (Kanto Chemical Co. Inc.; GR grade) was used as received.

Apparatus. In the conventional one-color laser excitation transient absorption experiment, an excimer laser (COMPex 102; KrF, 248 nm, 30 ns pulse duration) was used as a photolysis light source and a steady-state Xe lamp (Ushio UXL-300DO; 300W) was used as a probe light. In addition, for the TC-TA experiments, an excimer laser (COMPex 102; XeCl, 308 nm, 10 ns pulse duration), which was synchronously fired with the photolysis laser, was used as another excitation light source for the intermediates. The two laser beams were irradiated perpendicularly to the probe light. The probe light passed through a sample cell (NSG T-59FL-UV-10: 10 mm light path length) and a monochromator (Nikon P250) was detected with a photomultiplier tube (Hamamatsu; R928), converted into the voltage with a 50 or 500 Ω load resister, digitized with a digital oscilloscope (Sony Tektronix; TDS-380, 400 MHz, 2 GHz/Sampling), and transferred to a personal computer. The laser power dependence of the transient absorption was obtained by attenuating with optical filters.

An experimental setup of the TC-TRTL method is illustrated in Figure 1. The photolysis and excitation light sources were the same lasers as for the TC-TA measurement. The excitation light was focused inside the cell with a 150 mm focal length lens. The input laser power was varied with a neutral density linear-wedge filter (Corion 2161) and monitored by a silicon photodiode (Hamamatsu; S1336-5BQ). The photolysis light was irradiated uniformly to get rid of contamination of the heat released with the photolysis light irradiation. A cw He−Ne laser (Uniphase; 1103P, 3 mW) used as a probe for the thermal lens was spread with a 100 mm focal length lens, passed through the cell coaxially with the excitation beam, and sampled through the combination of a pinhole (Corion 2401; 300 μm diameter) and the monochromator. The TC-TRTL signals, detected with a photomultiplier tube (Hamamatsu; R928) and converted into the voltage with a 500 Ω load register, were dealt with the same procedure of the transient absorption measurement. The concentration of transient species, which was controlled by varying the dose of the photolysis laser or the concentration of the sample solution, was estimated by comparing the excitation laser intensity before and after the sample cell. All the sample solution was deoxygenated by bubbling with argon gas (stated purity 99.95%) saturated with the solvent vapor for half an hour before use and flowed in the cell to eliminate the influence of photoproducts. All measurements were carried out at room temperature. The confidence level for the values obtained in the experiment is 95%.

MO Calculations. Ab initio and DFT calculations were performed with the GAUSSIAN 03 program.[34] The transient rearranged isomers of BzCl in the ground state were optimized by the B3LYP/6-311G(d) level of theory. The normal-mode analysis was carried out at the same level. The energies at the B3LYP/6-311++G(3df,3pd) and MP2/6-311++G(3df,3pd) levels were obtained by using the B3LYP/6-311G(d) optimized geometries. Time dependent density functional theory (TD-DFT) calculation for the rearranged isomer of BzCl was also carried out at the B3LYP/6-311G(d) level.

Results and Discussion

Photolysis of BzCl and MeBzCls. Figure 2a shows transient absorption spectra of BzCl excited at 248 nm in hexane solution. A structured absorption band with peaks at 303 and 315 nm observed at 1.35 μs after the excitation completely disappeared within 173 μs, and a broad one remained in the spectral region between 280 and 340 nm. The structured band is identical with the reported one for Bz.[1] The structured band, observed in the transient absorption spectrum of dibenzyl ketone (DBK) excited at 308 nm, was also identical with the Bz spectrum, indicating that Bz was generated by the photolysis of DBK. However, the long-lived broad absorption band shown in Figure 2a was not observed in the transient absorption spectra of DBK. The fact strongly suggests that a chlorine atom (Cl) should be involved in the production of the long-lived species. In the previous paper the broad absorption band was tentatively assigned to a structural isomer of BzCl.[24] The contribution of a bromine atom to the generation of the photorearranged isomer was also suggested by excitation of 2-(bromomethyl)naphthalene in hexane.[27]

Time profiles of the transient absorption of BzCl in hexane monitored at 315 and 325 nm are shown in Figure 2b. The time profile monitored at 315 nm shows two components. The decaying one corresponds to the disappearance of Bz, while

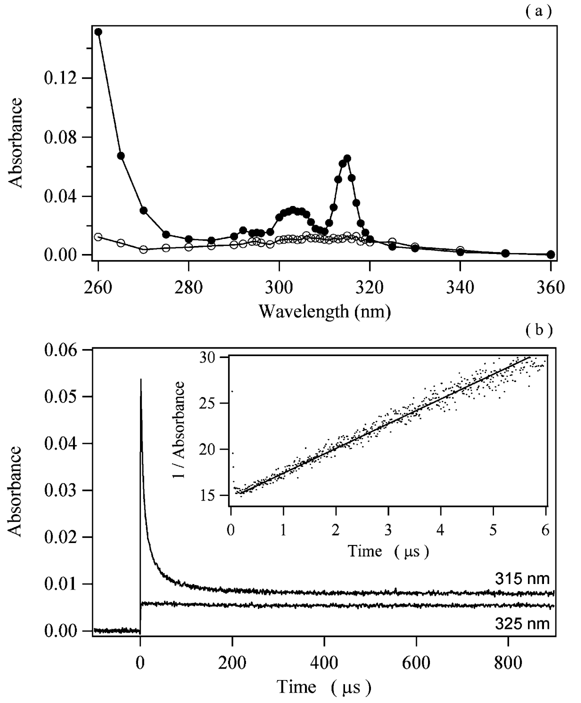

Figure 2. (a) Transient absorption spectra of BzCl in hexane observed at 1.35 (closed circle) and 173 μs (open circle) after the 248 nm excitation. A broad absorption band was observed in addition to the structured absorption band ascribable to benzyl radical. (b) Time profiles of the transient absorption of BzCl in hexane monitored at 315 and 325 nm. Reciprocal plots of absorbance of Bz against time, which was obtained by subtracting the contribution of the long-lived species from absorbance monitored at 315 nm, are shown in the inset. The solid line indicates the least-squares fitting.

the residual absorption is due to the long-lived species, which has the broad absorption band (cf. Figure 2a). The transient absorption monitored at 325 nm rose to a plateau within the laser pulse, revealing that the long-lived species is formed immediately after the excitation. If the long-lived species was the rearranged isomer produced by recombination of Bz and Cl atoms once free from the solvent cage, absorption due to the isomer should rise with the Bz decay. In the previous report,[24] the molecular structure of BzCl in the S_1 state was examined with MO calculations (MOPAC97). The Cl atom connected to the α-carbon moves onto the ortho-carbon while the C−Cl bond of the $-CH_2Cl$ group gets longer. This S_1 structure would result in the production of the rearranged isomer.

Reciprocal plots of net absorbance of Bz, which were obtained by subtracting the contribution of the long-lived species from absorbance monitored at 315 nm against time, are shown in the inset of Figure 2b. They were well fitted with a straight line obtained by the least-squares method, and the slope was determined to be $(2.2 \pm 0.1) \times 10^6$ s^{-1}. Therefore, Bz should mainly disappear with a bimolecular reaction under these experimental conditions. The rate constant of the bimolecular reaction was estimated to be $(2.0 \pm 0.1) \times 10^{10}$ M^{-1} s^{-1}, using the reported value of the molar absorptivity of 8.8×10^3 M^{-1} cm^{-1} at 316 nm for Bz in cyclohexane.[9] The reaction rate constant is comparable to the diffusion controlled rate of hexane (2.2×10^{10} M^{-1} s^{-1}).[35] The solid line in the inset of Figure 2b shows the analytical results with the reaction rate constant obtained above.

Figure 3 shows transient absorption spectra of *o*-, *m*-, and *p*-MeBzCls excited at 248 nm in hexane solution. Structured bands were observed at around 320 nm, and assigned to the corresponding benzyl radicals. Broad absorption bands, which have a longer lifetime than that of the benzyl radicals, were also observed. This indicates that the corresponding photorearranged isomers also should be produced by the photolyses of MeBzCls. The blue lines in insets of Figure 3 show time profiles of transient absorption monitored at 320 nm for *o*-, *m*-, and *p*-MeBzCls. The bimolecular reaction rate constants for the corresponding benzyl radicals were estimated with a similar procedure as for BzCl. The rate constants were again found to be diffusion controlled (ca. 2×10^{10} M^{-1} s^{-1}) under the assumption that the molar absorptivity at 320 nm (absorption band maximum) was 8800 M^{-1} cm^{-1}.

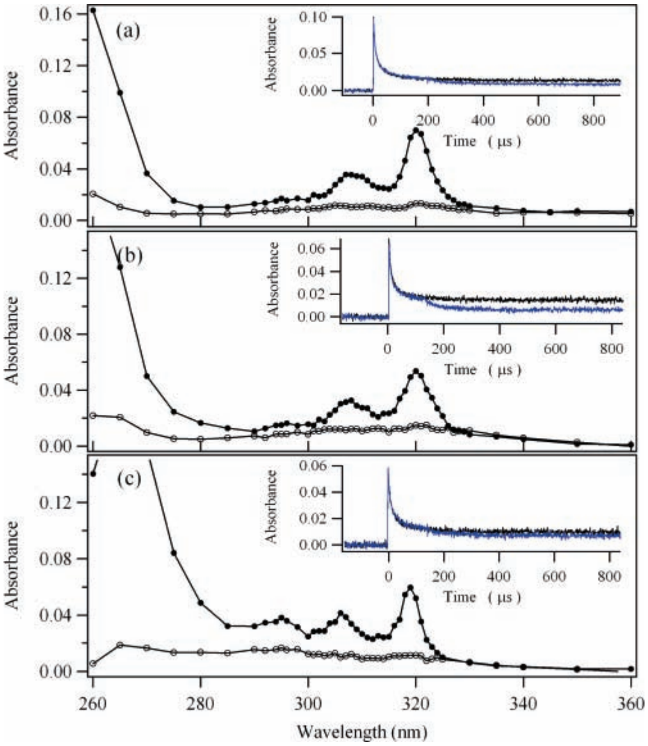

Figure 3. Transient absorption spectra of (a) *o*-MeBzCl, (b) *m*-MeBzCl, and (c) *p*-MeBzCl excited at 248 nm in hexane observed at 1.35 (closed circle) and 173 μs (open circle) after the excitation. Time profiles of the transient absorption monitored at 320 nm with (black lines) and without (blue lines) the irradiation of the 308 nm light are shown in the insets.

Excitation of the Long-Lived Species with TC-TA Measurement. In the TC-TA measurements, the excitation light (308 nm) was fired at 200 μs after the photolysis light (248 nm) irradiation to excite only the long-lived species, when almost all Bz should disappear with the bimolecular reaction described above (less than 1%). Time profiles of the TC-TA of BzCl in hexane monitored at 315 and 325 nm are shown as black lines in Figure 4, parts a and b, respectively. The time profiles of the transient absorption monitored at the corresponding wavelength are superimposed as blue lines for comparison. Both of the two time profiles definitely show the changes of absorbance after the excitation light irradiation, compared with the time profiles of transient absorption without the excitation light. In Figure 4b, bleaching was clearly observed, and did not recover within the time window (700 μs). It was found that the long-lived species disappeared immediately after the excitation of the 308 nm light, revealing the occurrence of a photochemical reaction. On the other hand, the time profile monitored at 315 nm (the inset of Figure 4a) shows a decaying component of transient absorption after the 308 nm light irradiation. These results indicate that photoexcitation of the long-lived species should

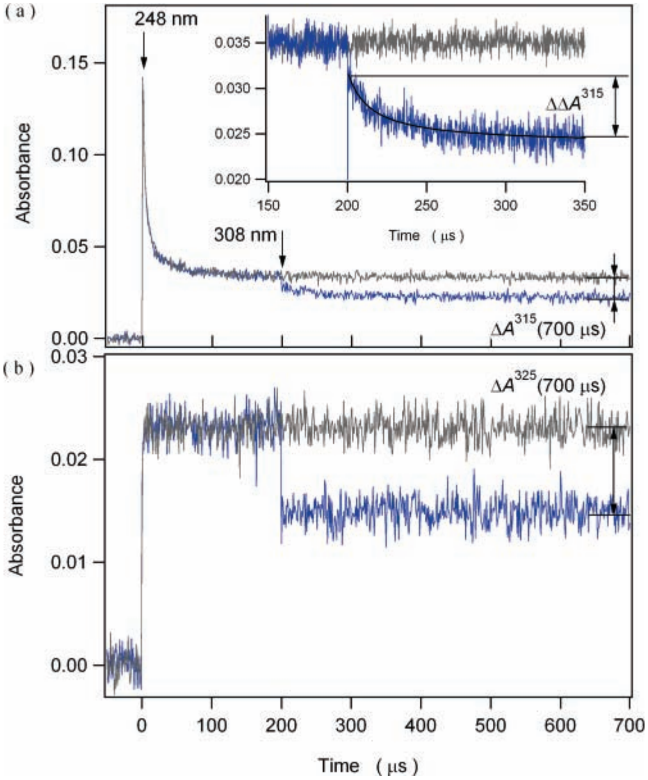

Figure 4. Time profiles of the TC-TA of BzCl in hexane monitored at (a) 315 nm and (b) 325 nm (black line). The 308 nm laser was fired at 200 μs after the 248 nm photolysis laser. The blue lines denote the transient absorption time profile monitored at the corresponding wavelength for comparison.

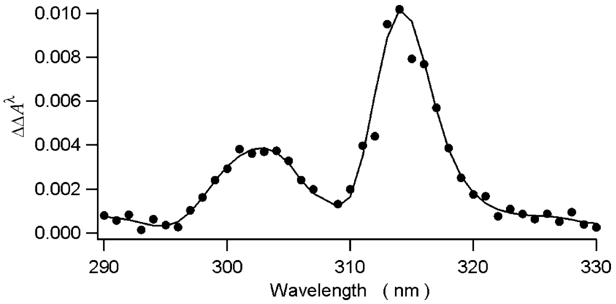

Figure 5. Plots of $\Delta\Delta A^{\lambda}$ vs wavelength. The spectral features are identical with that of Bz (see Figure 2a).

produce a new transient, which has absorption at 315 nm and the lifetime of several 10 μs.

The new transient was found to be produced within a laser pulse and disappear in 150 μs after the second laser excitation. To clarify the new transient, a difference spectrum was measured. The time-dependent absorbance change monitored at λ nm with the excitation laser is described as $\Delta A^{\lambda}(t)$, so absorbance of the new transient immediately after the excitation laser irradiation can be expressed as $\Delta\Delta A^{\lambda} = \Delta A^{\lambda}$ (200 μs) $-$ ΔA^{λ} (700 μs). Figure 5 shows the plots of $\Delta\Delta A^{\lambda}$ against the observed wavelength. The spectral features, the broad absorption band observed at around 302 nm and the strong band peak at 315 nm, are in excellent agreement with those of Bz (see Figure 2a). Furthermore, the decaying feature in the inset of Figure 4a was quite similar to that of the Bz radical. The solid line indicates the time course of Bz concentration obtained with the bimolecular reaction rate constant determined above. It becomes clear that the long-lived species should produce Bz after the excitation. In our previous report the photorearranged isomer of 2-(bromomethyl)naphthalene photoreacts to yield 2-naphthylmethyl radical.[27] This strongly suggests that the long-lived species should be the photorearranged isomer of BzCl. A schematic description of BzCl photoreaction is summarized in Scheme 1. The structure and excited dynamics for the isomer will be discussed later.

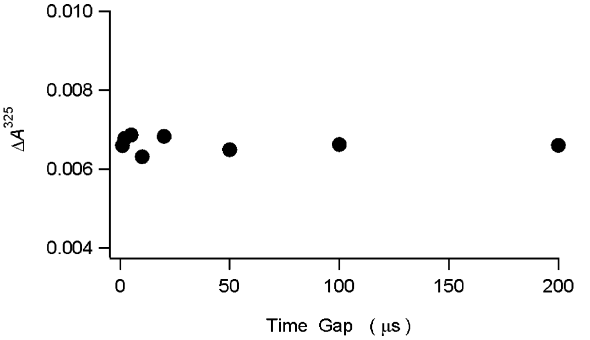

Figure 6. Plots of ΔA^{325} vs time gap between the photolysis and the excitation lasers.

SCHEME 1: A Schematic Description of BzCl Photoreaction: the Production and Photoreaction of the Rearranged Isomer

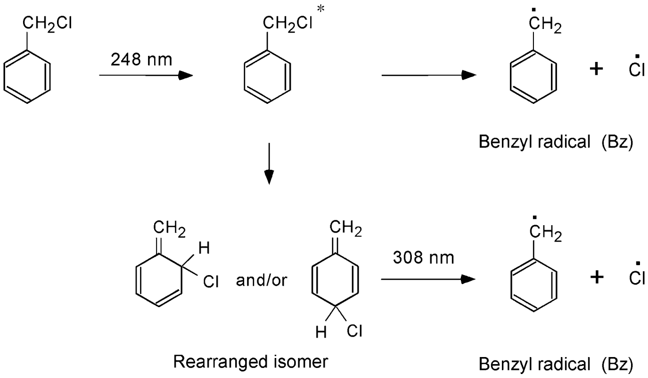

Figure 6 shows the ΔA^{325} vs time gap between the photolysis and the excitation lasers. The amount of bleaching was found to be constant in the time window examined. This suggests that the isomer should be formed within or immediately after the photolysis laser, not through the recombination reaction of free Bz radical and chlorine atom.

Time profiles of the TC-TA observed for *o*-, *m*-, and *p*-MeBzCls in hexane monitored at 315 nm are shown in the insets of Figure 3, parts a, b, and c, respectively (black lines). The time profiles without the irradiation of the second excitation light are also shown in the figures (blue lines) for comparison. The bleaching of the long-lived species and new transient absorption attributable to the corresponding radicals were observed by the 308 nm irradiation in the same way as BzCl, indicating the generation and photodissociation of the photorearranged isomers of *o*-, *m*-, and *p*-MeBzCls. These facts show that the methyl group at the ortho, meta, or para position would not affect the production and photoreaction of the isomers.

Molar Absorptivity and Photodissociation Quantum Yield of the Photorearranged Isomer of BzCl. The photoreaction of the photorearranged isomer was found to produce Bz. Therefore, the molar absorptivity of the isomer would be obtained with that of Bz and the absorbance change (ΔA) before and after the 308 nm laser irradiation.

$$\frac{\Delta\Delta A^{315}}{\Delta A^{315}(700\ \mu\text{s})} = \frac{\epsilon_{\text{Bz}}^{315}}{\epsilon_{\text{iso}}^{315}} \qquad (1)$$

Here, $\epsilon_{\rm Bz}^{315}$ and $\epsilon_{\rm iso}^{315}$ denote the molar absorptivities of Bz and the isomer at 315 nm, respectively. The $\Delta\Delta A^{315}/\Delta A^{315}(700\ \mu s)$ value was estimated to be 0.70 ± 0.05. With the literature value ($\epsilon_{\rm Bz}^{315} = 8.8 \times 10^3$ M^{-1} cm^{-1}) and the absorption spectrum of the isomer (see Figure 2a), the molar absorptivities of the photorearranged isomer at 315 and 325 nm were successfully estimated to be $(1.26 \pm 0.09) \times 10^4$ and $(8.5 \pm 0.6) \times 10^3$ M^{-1} cm^{-1}.

The laser power dependence and the concentration dependence of the isomer for the $|\Delta A^{325}|$ value monitored at 325 nm were examined. Good linearity was observed for each experiment, which indicates that photodissociation of the photorearranged isomer of BzCl is both single photon and unimolecular. Because the photoproduct, Bz, hardly absorbs the 325 nm light, the magnitude of the bleaching shown in Figure 3b, $|\Delta A^{325}|$, is expressed by

$$|\Delta A^{325}| = \epsilon_{\rm iso}^{325}\cdot\Delta C\cdot d;\ \Delta C = [\text{iso*}]\cdot\Phi_{\rm R} \qquad (2)$$

Here, [iso*] is the initial concentration of the photorearranged isomer excited by 308 nm, $\Phi_{\rm R}$ is the reaction quantum yield, and d is optical path length (1 cm). The [iso*] value was estimated by using naphthalene as an actinometer of which quantum yield of intersystem crossing to the lowest triplet state is reported to be 0.80 and the molar absorptivity is 24 500 M^{-1} cm^{-1} at 415 nm.[35] Therefore, the $\Phi_{\rm R}$ value was successfully obtained to be 0.54 ± 0.05. The relatively high reaction quantum yield of the photorearranged isomer would reflect very shallow or a repulsive potential surface for the lowest excited singlet state of the isomer. The excited-state character will be discussed later.

TC-TRTL Measurement for the Photorearranged Isomer of BzCl. As presented in the Introduction section, the TRTL technique can provide calorimetric and dynamical information. To elucidate the reaction dynamics of the excited isomers the TRTL measurements were carried out. Figure 7 shows the typical TC-TRTL signal of BzCl in hexane solution. The photolysis of BzCl at 248 nm causes the generation of both Bz and the photorearranged isomer as described above. To excite only the photorearranged isomer, the excitation light (308 nm) was fired at 150 μs after the photolysis light (248 nm) irradiation. No signal was observed when only one laser (248 or 308 nm) was irradiated, suggesting that the signal should result from the heat released from the excited state of the photorearranged isomer of BzCl.

The TC-TRTL signal rose immediately after the excitation light irradiation. The signal intensity, $U_{\rm iso}$, should be expressed by

$$U_{\rm iso} = K\cdot I_L\cdot(1-10^{-A_{\rm iso}})\cdot\alpha_{\rm iso} \qquad (3)$$

Here, K is an apparatus factor, which is governed by both the experimental alignment and thermoelastic properties of the solvent. $I_{\rm L}$ is the intensity of the excitation light. $A_{\rm iso}$ is the absorbance of the isomer at 308 nm. $\alpha_{\rm iso}$ is the heat conversion efficiency, which indicates the fraction of the energy released as heat against the photon energy absorbed. To obtain the $\alpha_{\rm iso}$ value, the $U_{\rm iso}$ values were measured with various laser intensities and concentrations of the photorearranged isomer. The concentration of the photorearranged isomer was controlled with the photolysis laser intensity or the concentration of the parent BzCl varied. The $A_{\rm iso}$ value at the time of the irradiation of the excitation light was determined by comparing the excitation laser power before and after the sample cell. Plots of the $U_{\rm iso}$ value against the excitation laser intensity ($I_{\rm L}$) showed good linearity. The slope of the straight line, $U_{\rm iso}/I_{\rm L}$, corresponds to $K(1-10^{-A_{\rm iso}})\alpha_{\rm iso}$. To obtain the K factor, we also performed the TRTL measurements for 2-hydroxybenzophenone in hexane, which is known as a calorimetric standard,[28] under exactly the same experimental condition. Thus, the $\alpha_{\rm iso}$ value is successfully determined to be 0.68 ± 0.02.

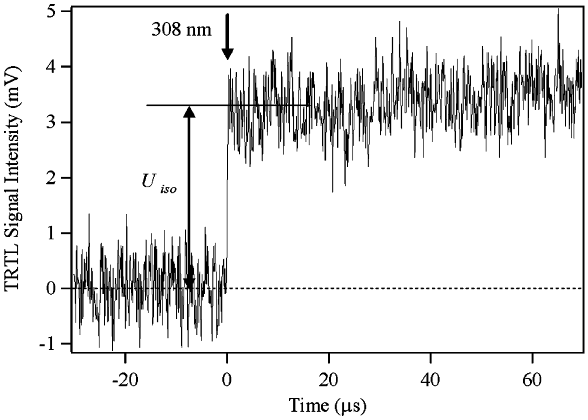

Figure 7. TC-TRTL signal of the long-lived species produced by the photolysis of BzCl in hexane solution. To excite only the longer-lived species, the excitation light (308 nm) was fired at 150 μs after the photolysis light (248 nm) irradiation. The signal did not appear when only one laser (248 or 308 nm) was irradiated.

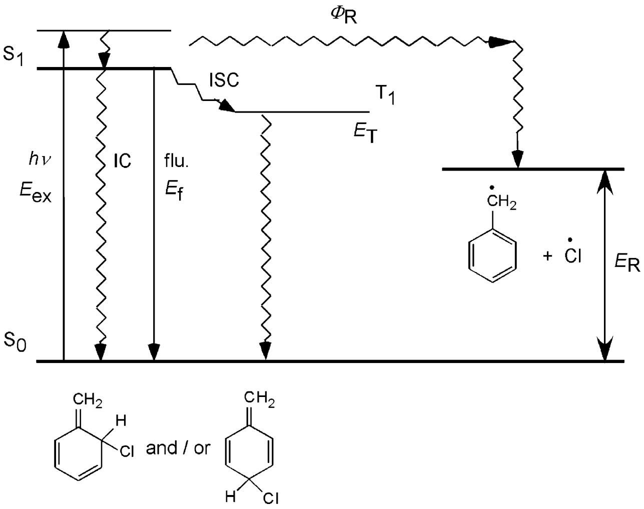

Figure 8. Schematic energy diagram of the reaction and relaxation processes from the excited state of the photorearranged isomer of BzCl.

The α value is, in general, described as[28,29]

$$\alpha = \left(E_{\rm ex} - \sum\Phi_{\rm f}E_{\rm f} - \sum\Phi_{\rm T}E_{\rm T} - \sum\Phi_{\rm R}E_{\rm R}\right)\Big/E_{\rm ex} \qquad (4)$$

where $E_{\rm ex}$ is the photon energy of the excitation light, $\Phi_{\rm f}$ is the emission quantum yield, $E_{\rm f}$ is the average energy of the emission, $\Phi_{\rm T}$ is the quantum yield of intersystem crossing, $E_{\rm T}$ is the energy of the lowest triplet state, and $\Phi_{\rm R}$ and $E_{\rm R}$ are the quantum yield and the heat of reaction, respectively (see Figure 8). In case of the photorearranged isomer, since the reaction quantum yield was fairly large and no emission and no slow-rising component in the TC-TRTL signal due to the excited triplet state were observed, eq 2 can be safely rewritten as

$$\Phi_{\rm R}E_{\rm R} = (1-\alpha)E_{\rm ex} \qquad (5)$$

Accordingly, the $E_{\rm R}$ value was determined to be 55 ± 5 kcal/mol, using $\Phi_{\rm R} = 0.54 \pm 0.05$, $\alpha = 0.68 \pm 0.02$, and $E_{\rm ex} = 93$

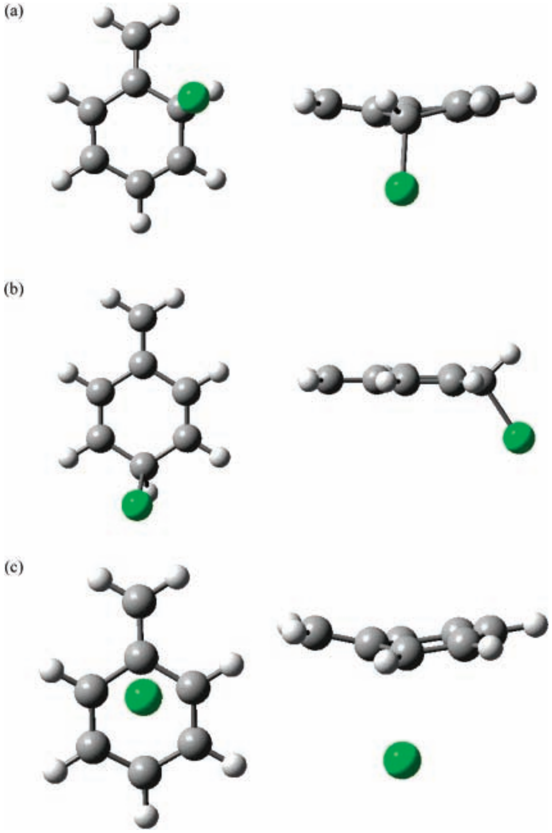

Figure 9. Ground-state geometries of (a) ortho- and (b) para-rearranged isomers of BzCl and (c) π-complex of Bz and Cl optimized by the B3LYP/6-311G(d) level of theory from the top and side view.

kcal/mol (the energy of the 308 nm light). The E_R value obtained should be regarded as the C−Cl bond energy of the isomer, which is found to be rather low compared with those values (70−90 kcal/mol) of the stable chlorinated compounds. The reaction dynamics will be discussed in the following section with the aid of MO calculations.

DFT and ab Initio Calculations of the Rearranged Isomer of BzCl. The ground-state geometries of the rearranged isomers of BzCl were optimized by calculation using the B3LYP/6-311G(d) level of theory. The optimized geometries of ortho- and para-rearranged isomers, in which a chlorine atom (Cl) is combined with a carbon atom in ortho and para positions, were determined (see Figure 9). Another optimized geometry, the π-complex of Bz and Cl, was also obtained (Figure 9c). The normal-mode analysis gave the result that the π-complex is a transition state between two ortho isomers, because it has one imaginary frequency (181i cm^{-1}) corresponding to the isomerization reaction coordinate. The stabilization energies of the ortho- and para-rearranged isomers and the π-complex against the isolated free radical pair of Bz and Cl were obtained to be 34.5, 38.1, and 15.2 kcal/mol at B3LYP/6-311++G(3df,3pd) and 41.6, 44.2, and 11.7 kcal/mol at MP2/6-311++G(3df,3pd), respectively, taking into account zero point energies. The stabilization energies for the ortho- and para-rearranged isomers derived by the calculation are consistent with the experimental results (55 ± 5 kcal/mol). This suggests evidence for generation of ortho- and/or para-rearranged isomers of BzCl by the photoexcitation of BzCl with 248 nm light in hexane solution (see Scheme 1).

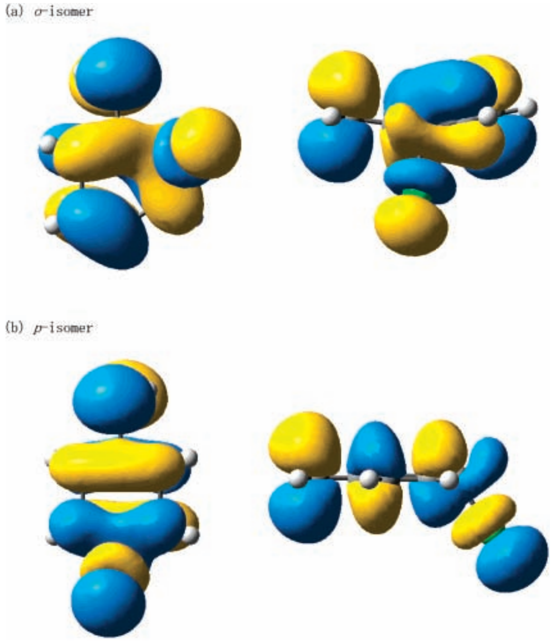

Figure 10. The description of the LUMOs for (a) ortho- and (b) para-rearranged isomers of BzCl. The LUMOs of the ortho- and para-rearranged isomers have antibonding character of their C−Cl bonds.

TD-DFT calculations of the ortho- and para-rearranged isomers of BzCl were also carried out. The S_1 state should be responsible for electronic transition to LUMO mainly. The LUMOs of the ortho- and para-rearranged isomers have antibonding character of their C−Cl bond (Figure 10), which are quite similar to the case of 1-isomer of 2-(bromomethyl)naphthalene reported previously.[27] The antibonding character of the C−Cl bond should result in the high photodissociation quantum yield of the photorearranged isomer of BzCl (Φ_R = 0.54 ± 0.05). These results also strongly suggest the generation and photodissociation of the ortho- and/or para-photorearranged isomers of BzCl.

Conclusion

Photoreaction of BzCl and *o*-, *m*-, and *p*-MeBzCls in hexane solution was studied at room temperature. The formation of the photorearranged isomers, whose lifetimes are considerably longer than that of the corresponding benzyl radicals, was clearly observed by the photoexcitation of *o*-, *m*-, and *p*-MeBzCls as well as BzCl. Further photoexcitation of the photorearranged isomers results in their photoreaction to yield the corresponding benzyl radicals. By quantitative TC-TA measurements, molar absorptivity ($\epsilon_{\mathrm{iso}}^{325}$) and photodissociation quantum yield (Φ_R) of the photorearranged isomer of BzCl were determined. The reaction quantum yield was found to be large (0.54 ± 0.05). With TC-TRTL measurements, the heat of reaction of the photorearranged isomer (E_R) was successfully obtained (55 ± 5 kcal/mol). These experimental results such as high reactivity and heat of reaction for the excited isomers were well supported by the MO calculations. It was demonstrated that the TC-TRTL technique coupled with the TC-TA was a powerful tool to elucidate reaction dynamics of the metastable species in the excited state such as the rearranged isomer of benzyl chlorides and to obtain calorimetric information.

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