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Dihydrophenanthrene-Type Intermediates during Photoreaction of *trans*-4′-Benzyl-5-styrylfuran

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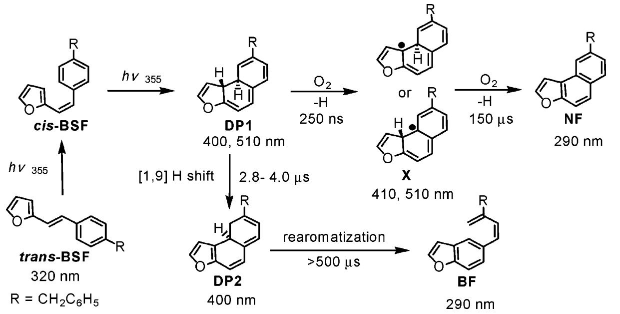

Photoreaction of *trans*-4′-benzyl-5-styrylfuran (*trans*-**BSF**) has been studied by the 355-nm laser flash photolysis (LFP) in CH_2Cl_2 using a Nd^{3+}:YAG laser (30 ps, 5 mJ $pulse^{-1}$ or 5 ns, 30 mJ $pulse^{-1}$). Transient fluorescence and absorption spectra assigned to the singlet excited *trans*-**BSF** were observed during the 30-ps LFP, whereas a transient absorption spectrum with two peaks at 400 and 510 nm, assigned to the *trans*-fused dihydrophenanthrene (DHP)-type intermediate (**DP1**), was observed during the 5-ns LFP. It is clearly suggested that a two-photon absorption process is involved in the formation of **DP1**. The first photoreaction is the photoisomerization of *trans*-**BSF**, which occurs to give *cis*-**BSF**. The second photoreaction process is photocyclization of *cis*-**BSF**, which occurs to give **DP1** decaying with the half lifetime ($\tau_{1/2}$) of 2.8−4.0 μs to produce another DHP-type intermediate (**DP2**) with an absorption peak at 400 nm in the absence of O_2, through [1,9]-hydrogen shift. **DP2** decayed with $\tau_{1/2}$ > 500 μs to give the product through aromatization. In O_2-saturated CH_2Cl_2, **DP1** decayed with $\tau_{1/2}$ = 250 ns to give a radical intermediate (**X**) with two peaks at 410 and 510 nm, through hydrogen abstraction of **DP1** by O_2. **X** decayed with $\tau_{1/2}$ = 150 μs to give the product through successive hydrogen abstraction.

Introduction

Photochemical reactions of stilbene-type compounds are well documented. The oxidative cyclization occurs to form phenanthrene-type compounds as one of the major pathways[1−3] and can be utilized for organic synthesis.[4] The mechanistic studies have not been fully carried out, although the transient absorption of the intermediates dihydrophenanthrenes (DHPs) is suggested to be detected in solution in the 400−500 nm region. The isolation of DHPs is very difficult because of the rapid oxidative hydrogen abstraction to give phenanthrene-type compounds or reverse ring opening to the starting stilbene-type compounds. Several attempts to isolate the stable intermediates have been reported. Muszkat and Fischer photolyzed 1,1′,3,3′,5,5′-hexamethylstilbene and 1,2-diphenylcyclopentene and obtained the corresponding DHPs in 21% and 67% yields, respectively.[5] Blackburn et al. reported that DHPs may be produced from photo-

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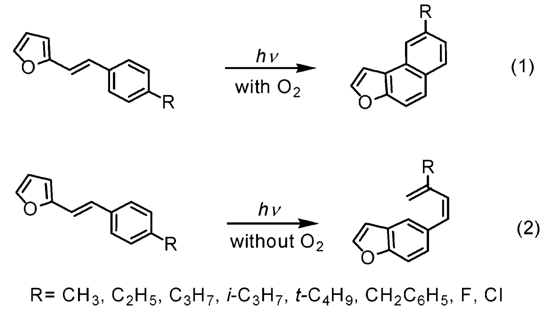
SCHEME 1



cyclization of styrylnaphthalenes based on the steric arguments.[6] Although DHPs were observed to have the relatively long lifetime in solution, they were not isolable. Doyle et al. studied UV absorption spectra of the DHP-type intermediates during the photolysis of diethylstilbestrol.[7]

Recently, one of our authors reported the novel and efficient photochemical reaction of styrylfurans.[8] The products were the corresponding cyclized products in the presence of oxygen, whereas they were the corresponding benzo[*b*]furans with a buta-1,3-diene moiety in the absence of oxygen (Scheme 1). It is suggested that the two DHP-type intermediates (**DP1** and **DP2**) are involved in this photochemical reaction. It is suggested that the presence of the furan ring must affect the different reaction mechanism from that of the photoreaction of stilbene.[8] Attempts to isolate these intermediates were not successfully carried out.

In this paper, we seek to elucidate the intermediates during the irradiation of *trans*-4′-benzyl-5-styrylfuran (*trans*-**BSF**, R= CH$_2$C$_6$H$_5$ for the starting olefin of eqs 1 and 2 in Scheme 1) in CH$_2$Cl$_2$ using a Nd^{3+}:YAG laser at 355 nm. It is suggested that, in the presence of oxygen, *trans*-**BSF** affords 8-benzyl-naphtho[2,1-*b*]furan (**NF**, R= CH$_2$C$_6$H$_5$ for the product of eq 1 in Scheme 1),[9−15] whereas in the absence of oxygen, it affords 5-(3-benzyl-buta-1,3-dienyl)-benzofuran (**BF**, R= CH$_2$C$_6$H$_5$ for the product of eq 2 in Scheme 1) in a high yield (95%).[8] We report here on the mechanism for the photoreaction of *trans*-**BSF** in the absence and presence of oxygen during picosecond or nanosecond laser flash photolysis (LFP).

Experimental Section

Material and General. *trans*-4′-Benzyl-5-styrylfuran (*trans*-**BSF**) was prepared from 2-furaldehyde and (4-benzyl)benzyl chloride through a Wittig reaction: mp 73−74 °C.[8] The products 8-benzyl-naphtho[2,1-*b*]furan (**NF**) and 5-(3-benzyl-buta-1,3-dienyl)benzofuran (**BF**) were obtained by irradiation of *trans*-**BSF** in oxygen-saturated and degassed CH$_2$Cl$_2$ solutions, respectively, in a Pyrex tube using Rayonet reactor (350 nm) for a few hours. These products were isolated by column chromatography on silica gel. No other byproducts were observed in the crude ^{1}H NMR. They were also identified by HR-MS.[8] Dichloromethane (CH$_2$Cl$_2$) was purchased (spectroscopic grade) and used as solvent without further purification.

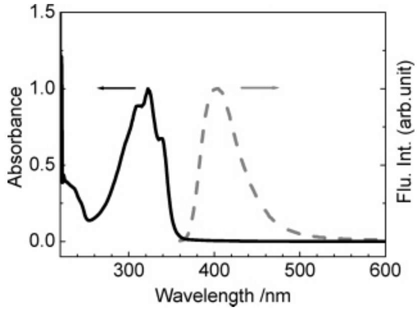


FIGURE 1. Absorption and fluorescence spectra of *trans*-**BSF** in CH$_2$Cl$_2$.

UV spectra were measured in CH$_2$Cl$_2$ by a UV−vis spectrometer with a transparent rectangular cell made from quartz (1.0 × 1.0 × 4.0 cm^3, path length of 1.0 cm). Fluorescence spectra were measured by a spectrofluorometer.

Laser Flash Photolysis. Laser flash photolysis (LFP) experiments were carried out using the third harmonic oscillation (355 nm) from a mode-locked Nd^{3+}:YAG laser (30-ps fwhm, 10 Hz) seeded by a picosecond diode laser (1064 nm, 5-ps, 100 MHz) and a Nd^{3+}:YAG laser (355 nm, 5-ns fwhm) as an excitation source.[16−21] The monitor light was obtained from a 450-W Xe lamp synchronized with the laser flash. The laser beam was perpendicular to the monitor light. The intensity of the monitor light source was detected using a silicon detector. The signal from the silicon detector was digitalized by an oscilloscope and transmitted to a personal computer via the interface. Transient absorption spectra were measured by a streak camera equipped with a CCD camera. The concentration of *trans*-**BSF** was adjusted to have an absorbance of 1.0 at 355 nm (5.0 × 10^{-4} M).

Results and Discussion

Absorption and Fluorescence Spectral Measurements. Figure 1 shows the absorption and fluorescence spectra of *trans*-**BSF** in CH$_2$Cl$_2$ solution. The ground-state absorption peak was observed at 320 nm, and the fluorescence peak was at 410 nm.

Picosecond Laser Flash Photolysis. A transient absorption spectrum with a peak at 530 nm was observed at 100 ps after a 30-ps laser flash during the LFP of *trans*-**BSF** in Ar-saturated CH$_2$Cl$_2$ as shown in Figure 2. At 1 ns after the laser flash, the peak at 530 nm disappeared (Figure 2). The half lifetime ($\tau_{1/2}$) of the

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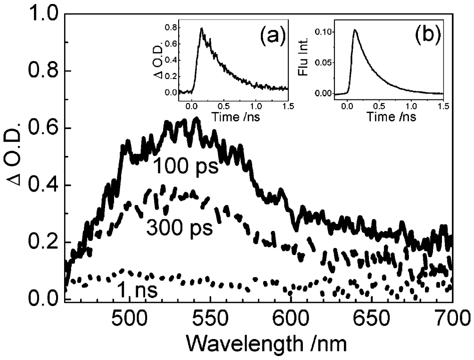

FIGURE 2. Transient absorption spectra observed at 100 ps, 300 ps, and 1 ns after a 30-ps 5-mJ laser flash during the 355-nm LFP of *trans*-**BSF** in Ar-saturated CH_2Cl_2. Insets: time profiles of the transient absorption at 530 nm (a) and fluorescence intensity at 410 nm (b) in the time scale of 1.5 ns.

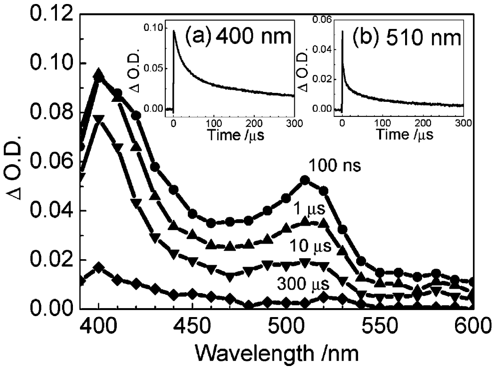

FIGURE 3. Transient absorption spectra observed at 100 ns, 1 μs, 10 μs, and 300 μs after a 5-ns 30-mJ laser flash during the 355-nm LFP of *trans*-**BSF** in Ar-saturated CH_2Cl_2. Insets: time profiles of the transient absorption at 400 (a) and 510 nm (b) in the time scale of 300 μs.

transient absorption peak was 400 ps (Figure 2a). A fluorescence spectrum was observed to have a peak at 410 nm and $\tau_{1/2}$ = 320 ps (Figure 2b). In th case of the O_2-saturated solution, a similar transient absorption was observed with $\tau_{1/2}$ = 370 ps during the 30-ps LFP (Supporting Information, Figure S2), and the similar fluorescence spectrum was observed. Therefore, the observed transient absorption is reasonably assigned to the S−S absorption of *trans*-**BSF** in the lowest excited singlet state. The $\tau_{1/2}$ value in O_2-saturated solution was 370 ps, which is 14% longer than that in Ar-saturated solution. Since the difference is not significant under the present 30-ps LFP experiments, the $\tau_{1/2}$ value is considered to be almost equivalent in Ar-saturated and O_2-saturated solutions.

Nanosecond Laser Flash Photolysis. A transient absorption spectrum with two peaks at around 400 and 510 nm was observed immediately after a 5-ns laser flash during the LFP of *trans*-**BSF** in Ar- or O_2-saturated CH_2Cl_2 as shown in Figures 3 and 4, respectively. When the laser intensity (I) was low (7.0 mJ), the optical density of the transient absorption peaks (ΔOD) was low (<0.01). On the other hand, when it was high (30 mJ), the transient absorption peaks were observed with high ΔOD of 0.04−0.1 as shown in Figures 3 and 4. ΔOD increased with increasing of I (Supporting Information, Figure S3a). The log−log plots of ΔOD vs I gave a liner line with the slope = 1.5 (Supporting Information, Figure S3b). It is clearly suggested that two-photon absorption process must be involved in the formation of species with the absorption. It has been reported that the photocyclization of stilbene-type compounds occurs from the *cis*-isomer, which is consequently excited with irradiation to yield the DHP intermediate.[1−3] Similarly, it is suggested that the *cis*-isomer is generated through the first photoisomerization process and the transient species and photoproducts are generated from the *cis*-isomer through the successive second photocyclization process during the nanosecond LFP (totally two-photon process).

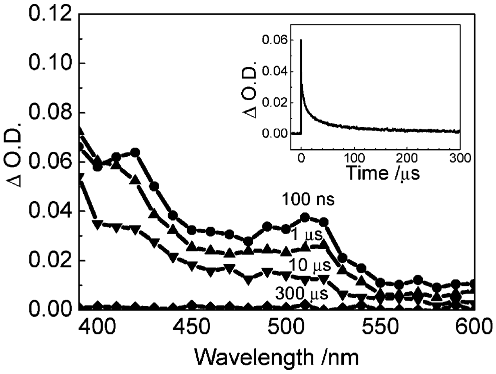

FIGURE 4. Transient absorption spectra observed at 100 ns, 1 μs, 10 μs, and 300 μs after a 5-ns 30-mJ laser flash during the 355-nm LFP of *trans*-**BSF** in O_2-saturated CH_2Cl_2. Inset: time profile of the transient absorption at 510 nm in the time scale of 300 μs.

A transient absorption spectrum with two peaks at 400 and 510 nm was observed at 100 ns after a laser flash during the 5-ns LFP of *trans*-**BSF** in Ar-saturated CH_2Cl_2 as shown in Figure 3. The absorption peak at 400 nm remained even at 300 μs after the laser flash. The time profile of the transient absorption at 400 nm showed two component decays: short-lived and long-lived components with $\tau_{1/2}$ = 35 μs and >500 μs, respectively (Figure 3, inset a). Two component decays were also shown in the transient absorption at 510 nm: short-lived and long-lived components with $\tau_{1/2}$ = 2.8 μs and >500 μs (Figure 3, inset b). On the other hand, only the short-lived transient species with $\tau_{1/2}$ = 4.0 μs was observed at 580 nm. These results suggest that the short-lived transient species with two peaks at 400 and 510 nm converts in the 2.8- to 4.0-μs time scale to the long-lived species with a peak at 400 nm and $\tau_{1/2}$ > 500 μs in the absence of oxygen. The apparent $\tau_{1/2}$ = 35 μs at 400 nm is due to the overlapping of decay of the short-lived transient species and formation and decay of the long-lived transient species.

Figure 4 shows the transient absorption spectrum with two peaks at 410 and 510 nm observed at 100 ns after a laser flash during the 5-ns LFP of *trans*-**BSF** in O_2-saturated CH_2Cl_2. The decay of the spectrum did not depend on the wavelength. The time profile of the transient absorption at 510 nm showed two component decays: short-lived and long-lived components with $\tau_{1/2}$ = 250 ns and 150 μs, respectively (Figure 4, inset). It is clear that the lifetimes of the transient species are different from each other in the absence and presence of oxygen, indicating the fast reaction of the transient species with oxygen.

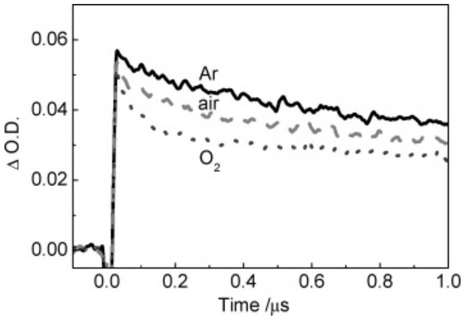

FIGURE 5. Time profiles of the transient absorption at 510 nm in the time scale of 1.0 μs during the 355-nm, 5-ns, and 30-mJ LFP of *trans*-**BSF** in Ar-, air- and O_2-saturated CH_2Cl_2.

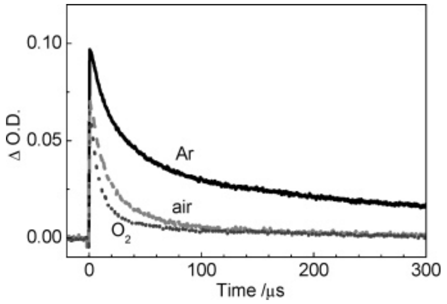

FIGURE 6. Time profiles of transient absorption at 400 nm in the time scale of 300 μs during 355-nm, 5-ns, and 30-mJ LFP of *trans*-**BSF** in Ar-, air-, and O_2-saturated CH_2Cl_2.

Effects of Dissolved Oxygen. Figure 5 shows the time profile of the short-lived component with a peak at 510 nm during the LFP of *trans*-**BSF** in Ar-, air-, or O_2-saturated CH_2Cl_2. It was observed that the lifetime of the short-lived component decreased with increase of the concentration of dissolved oxygen. Therefore, this short-lived component is assigned to the *trans*-fused DHP-type intermediate (**DP1**)[8] because hydrogen abstraction of DHP occurs with dissolved oxygen.[3] It is also reasonably explained that the absorption spectrum of DHP, which is the similar to the transient species observed during the photoirradiation of *trans*-stilbene, has a very broad absorption band centered at 455 nm.[3]

Figure 6 shows both the short-lived **DP1** and long-lived component observed at 400 nm. The $\tau_{1/2}$ value of the long-lived component was different in the absence and presence of oxygen. In the absence of oxygen, a long-lived component observed at 400 nm showed that $\tau_{1/2}$ was >500 μs. It is suggested that a long-lived intermediate is assigned to another DHP-type intermediate (**DP2**), which is generated from the [1,9]-hydrogen shift reaction of **DP1**.[8] The decay of **DP2** in the time scale of >500 μs corresponds to the formation of **BF** with an absorption peak at 290 nm as the stable product (Supporting Information, Figure S1), through aromatization of **DP2**. The long-lived intermediate with $\tau_{1/2}$ > 500 μs was observed at 400 nm only under Ar-saturated condition. Therefore, it is reasonably assigned to **DP2** according to the mechanism proposed previously.[8] This result corresponds to the absorption spectra of various DHP-type intermediates that are observed in the region of 400−500 nm.[7]

On the other hand, in the presence of oxygen, the long-lived component with $\tau_{1/2}$ = 150 μs was observed with two peaks at 410 and 510 nm. It could be assigned to be a radical intermediate (**X**) generated from hydrogen abstraction of **DP1** by dissolved oxygen. Similar hydrogen abstraction of **X** by dissolved oxygen occurs to give **NF** with an absorption peak at 290 nm as the stable product (Supporting Information, Figure S1). It is suggested that the intermediate DHPs-type compound is first generated from the photochemical cyclization of a *cis*-isomer and that two-step successive abstractions of tertiary hydrogen atoms from DHPs by oxygen occurs to give phenanthrene-type aromatic hydrocarbons. It is also assumed that the first hydrogen abstraction from DHPs occurs to produce a radical intermediate.[3] It is well-known that *trans-cis* isomerization of a *trans*-styrylfuran occurs to give a *cis*-isomer and that photochemical cyclization of a *cis*-isomer occurs to give **NF** as the stable product in the presence of oxygen.[9−15] Therefore, cyclization of a *cis*-isomer (**DP1**) and formation of a radical intermediate for styrylfuran (**X**) are also assumed. In the present work, the transient absorption with two peaks at 410 and 510 nm observed in O_2-saturated solution was consisted of two components: short-live (250 ns) and long-lived (150 μs) components. The short-lived component was assigned to **DP1**. Because the stable product **NF** has no absorption at 410 and 510 nm, the long-lived component is assigned to **X**. The electronic characters of **DP1** and **X** are expected to be similar each other, although **X** has a *p*-electron through the hydrogen abstraction from **DP1**. Therefore, it is reasonable that both **DP1** and **X** have similar absorption peaks at 400−410 and 510 nm. Similar radical intermediates are known to have absorption in the visible region; for example, it has been reported that 10,11-dihydrodibenzo[*a,d*]cycloheptene radical has absorption peaks at ∼360, 410, and 430 nm.[22] In addition, the lifetimes of radicals similar to **X** are reported to be in microsecond order.[23] It has also been reported that dissolved oxygen can undergo the abstraction of hydrogen atoms from radical intermediates similar to **X** giving phenanthrene analogues as the stable products.[24,25]

Mechanism. The results obtained in the present LFP study are consistent with the photochemical reaction mechanism of *trans*-**BSF** based on the product analysis.[8] The photochemical reaction mechanism involving intermediates (*cis*-**BSF**, **DP1**, **DP2**, and **X**) in the absence and presence of oxygen is summarized in Scheme 2. The absorption spectrum with a peak at 530 nm was observed during the 30-ps LFP to be assigned to *trans*-**BSF** in the lowest excited singlet state because its lifetime was almost same as that of the fluorescence. It is found that dissolved oxygen has little influence on the transient behavior of *trans*-**BSF** in the ps-ns time region.

On the other hand, the transient absorption with two peaks at around 400 and 510 nm was consisted of two components during the 5-ns LFP in both Ar- and O_2-saturated CH_2Cl_2. When the laser intensity was low, the optical density of the transient absorption was not sufficiently large to be detected. The optical density

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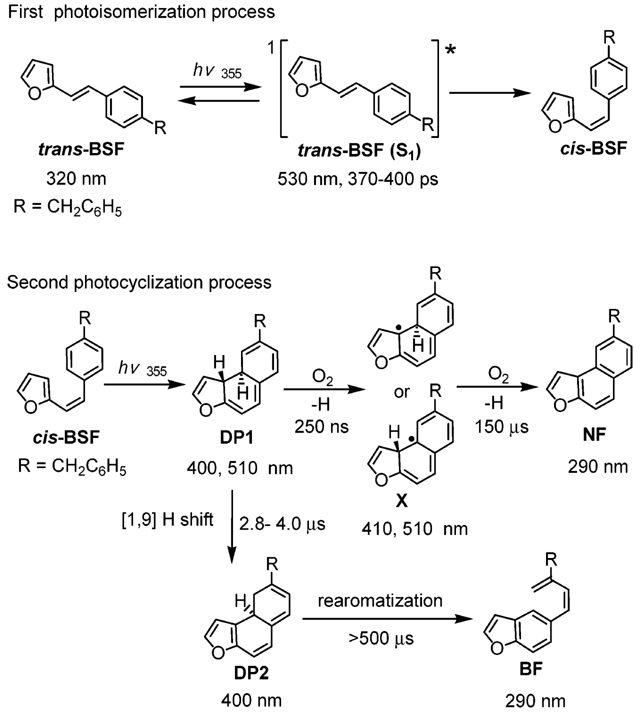
SCHEME 2



increased with increase of the laser intensity in a second order relation. Therefore, it is considered the transient absorption observed during the 5-ns LFP is generated through the two-photon absorption. The short-lived component is assigned to **DP1** with $\tau_{1/2}$ affected strongly by the concentration of dissolved oxygen: $\tau_{1/2} = 2.8-4.0$ μs and 250 ns in Ar- and O_2-saturated CH_2Cl_2, respectively. The long-lived component was observed at 400 nm with $\tau_{1/2}$ of >500 μs in Ar-saturated CH_2Cl_2 and assigned to **DP2**, suggesting the [1,9]-hydrogen shift of **DP1** occurs to give **DP2**, which undergoes aromatization to give **BF** as the stable product. On the other hand, the long-lived component was observed with two peaks at 410 and 510 nm and $\tau_{1/2} = 150$ μs during the LFP in O_2-saturated CH_2Cl_2, assigned to **X** generated from the hydrogen abstraction of **DP1** by dissolved oxygen. The successive hydrogen abstraction from **X** by dissolved oxygen occurs to give **NF** as the stable product. Although we attempted to trap these intermediates at low temperature, we could not succeed. However, the experimental results are reasonably explained by the reaction mechanism shown in Scheme 2.

It should be noted that the transient absorption spectra of DHP-type intermediates, **DP1** and **DP2**, were observed during the LFP of *trans*-**BSF** in the absence of oxygen. Moreover, **X** was also observed in the presence of oxygen. Since the transient absorption of DHP cannot be easily detected during the LFP of *trans*-stilbene, the presence of the furan ring must be responsible for stabilization of **DP1**, **DP2**, and **X** to be detected by the transient absorption measurement.[8]

Conclusions

The photochemical reaction of *trans*-**BSF** in Ar-, air-, and O_2-saturated CH_2Cl_2 has been studied by ps and ns LFP measurements. Although the intermediate DHPs were extremely unstable to be isolated, transient absorption spectra of two DHP-type intermediates (**DP1** and **DP2**) were observed together with the radical intermediate **X** generated from hydrogen abstraction of **DP1** in the presence of oxygen. On the basis of the present LFP experiments and product analysis, the photoreaction mechanism was confirmed. Photoisomerization of *trans*-**BSF** initially occurs through *trans*-**BSF** in the lowest excited singlet state to give *cis*-**BSF**, which is successively excited to give **DP1** with two peaks at 400 and 510 nm. The [1,9]-hydrogen shift of **DP1** occurs in the time scale of 2.8−4.0 μs to give **DP2** with a absorption at 400 nm, which undergoes aromatization in the time scale >500 μs to give **BF** as the stable product in the absence of oxygen. The hydrogen abstraction of **DP1** by oxygen occurs in the time scale of 250 ns to give **X** with two peaks at 410 and 510 nm in O_2-saturated CH_2Cl_2 solution. Successive hydrogen abstraction of **X** by oxygen occurs in the time scale of 150 μs to give **NF** as the stable product. It should be emphasized that the presence of the furan ring is responsible for stabilization of **DP1**, **DP2**, and **X** to be detected by the transient absorption measurement.

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Supporting Information Available: Ground-state absorption spectra, transient absorption spectra, plot of the optical density of the transient absorption (ΔOD) at 510 nm vs laser intensity (*I*), the chemical yields for the photochemical reaction of *trans*-**BSF** in N_2- and O_2-saturated CH_2Cl_2 and ^1H NMR spectral data of **NF**. This material is available free of charge via the Internet at http://pubs.acs.org.

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