Selective Carbon-Bromine Bond Fission Induced by Non-Resonant Two-Photon (NRTP) Excitation of *trans*-4-Bromostilbene

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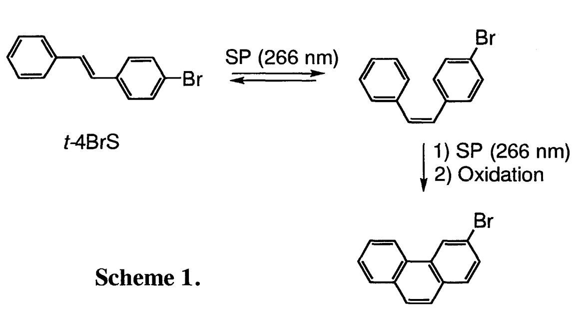
Non-resonant two-photon (NRTP) excitation of a 1,4-dioxane solution of *trans*-4-bromostilbene induces selective homolytic carbon-bromine bond fission, in contrast to the corresponding single-photon (SP) excitation, where the *cis-trans* isomerization is predominant.

We have recently reported that non-resonant two-photon (NRTP) excitation induces dramatic change of the photochemical reaction pathways of several organic compounds in solution from the conventional single-photon (SP) excitation.[1] Typically, the NRTP excitation of hexane solutions of α,ω-diphenylpolyenes such as stilbenes and *trans*-1,4-diphenylbutadiene[1b,c] induces selectively *cis-trans* isomerization, while the SP excitation yields several byproducts in addition to the isomerization.[2,3] We have applied the NRTP method to *trans*-4-bromostilbene (*t*-4BrS) and found a highly selective carbon-bromine bond fission in 1,4-dioxane, in contrast to the SP excitation, which induces the *trans-cis* isomerization predominantly, while the prolonged SP irradiation yields 3-bromophenanthrene (BrPhen) via the intramolecular cyclization.[3d] This finding constitutes the first example of the selective photoreaction by the NRTP excitation except for the *cis-trans* isomerization of α,ω-diphenylpolyenes, suggesting the biradical nature of the two-photon allowed excited state.

When a 1,4-dioxane solution of *t*-4BrS (3.5 x 10^{-3} M), which was purified by recrystallization from ethanol before use, was irradiated at room temperature with 266 nm pulsed light (the fourth harmonic of a Nd:YAG laser, 1.2 MW/cm^2, pulse width ~4 ns, 10 Hz) for 45 min, *cis*-4-bromostilbene (*c*-4BrS), 3-bromophenanthrene (BrPhen), and *t*-stilbene (*t*-S) were formed in the yields of 29%, and 8%, and 1.2%, respectively, together with the recovered *t*-4BrS (46%), as determined by gas chromatography. The time course of the product distribution is shown in Figure 1. These results are in good accord with a previous SP photochemistry of *t*-4BrS using a Hg arc lamp.[3d]



Scheme 1.

On the other hand, quite different photoreactions were observed when a 1,4-dioxane solution of *t*-4BrS (3.5 x 10^{-3} M) was irradiated with 532 nm pulsed light (the second harmonic of a Nd:YAG laser, 400 MW/cm^2, pulse width ~6 ns, 10 Hz) at room temperature. Thus, irradiation of a 1,4-dioxane solution of *t*-4BrS produced selectively *unsubstituted trans*-stilbene (*t*-S), together with a small amount of *c*-4BrS as shown in Figure 2 (a). The yields of *t*-S, *c*-4BrS and the recovery of *t*-4BrS after 180 min irradiation were 37%, 1.0%, and 32%, respectively. The formation efficiency[4] of *t*-S increased in proportion to almost the square of the light intensity as shown in Figure 2 (b).

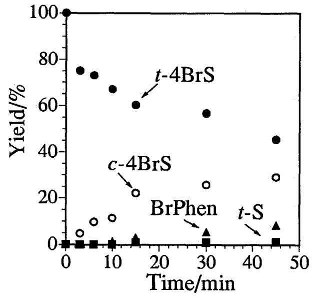
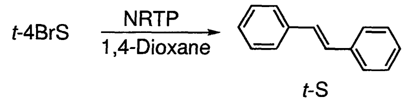


Figure 1. Time course of the product distribution during irradiation of *t*-4BrS with 266 nm laser pulses in 1,4-dioxane.



(1)

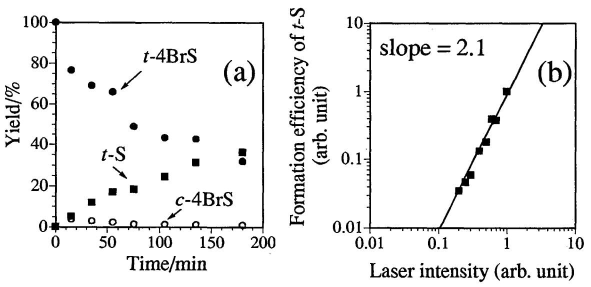


Figure 2. (a) Time course of the product distribution during irradiation of *t*-4BrS with 532 nm laser pulses in 1,4-dioxane. (b) Square dependence of the relative formation efficiency of *trans*-stilbene (*t*-S) on the incident laser intensity (532 nm) for NRTP excitation of *t*-4BrS.

In order to confirm the two-photon nature of the *t*-S formation *via* the excitation of *t*-4BrS using the 532-nm light, we have examined (1) a photoreaction of *t*-4BrS by direct singlet-triplet excitation with a CW Ar$^+$ laser and (2) the wavelength dependence of the efficiency of *t*-S formation from *t*-4BrS, which is compared with the two-photon absorption spectrum of *t*-4BrS obtained by the two-photon fluorescence (TPF) method.[1c,5]

Irradiation of a 1,4-dioxane solution of *t*-4BrS with CW 514 nm light (1 W) from Ar^+ laser did not yield *t*-S at all, but gave a very clean mixture of *t*-4BrS and *c*-4BrS; after 900 min irradiation, *c*-4BrS and *t*-4BrS were found to be 65% and 34%, respectively. The triplet states of *trans*- and *cis*-4-bromostilbenes would be related to the selective *cis-trans* isomerization, since the direct singlet-triplet absorption of stilbenes is observed at around 500 nm.[6] The results also indicate that the triplet state of *t*-4BrS does not produce *t*-S via the photodissociation of the C-Br bond.

Irradiation of *t*-4BrS using pulsed light from 460 to 630 nm (80 MW/cm^2, pulse width 3 ns, 10 Hz)[7] gave *t*-S as the major product, in similar to the irradiation with the pulsed 532-nm light. Figure 3(a) shows a plot of the formation efficiency of *t*-S[4] vs a half of the wavelength of the incident laser light ($\lambda_t/2$). The action spectrum showed a maximum at around λ_t = 490 nm. The feature is in good agreement with the two-photon absorption spectrum in 1,4-dioxane obtained by monitoring dependence of the $S_1 \rightarrow S_0$ fluorescence intensity at 350 nm on $\lambda_t/2$ as shown in Figure 3.[8] The above results evidence that the selective carbon-bromine bond fission occurs from the two-photon excited state.[9]

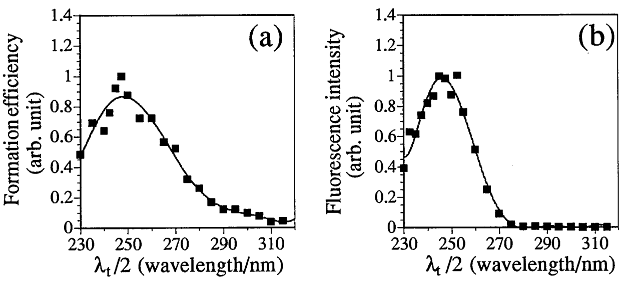


Figure 3. The wavelength dependence of (a) formation efficiency of *t-S* from *t*-4BrS and (b) relative fluorescence intensity of *t*-4BrS monitored at 350 nm.

A plausible mechanism for formation of *t*-S during the NRTP irradiation of *t*-4BrS is the spontaneous C-Br bond fission from the excited state to give *t*-stilben-4-yl radical, which abstracts hydrogen from a solvent molecule. In order to verify this mechanism, a similar NRTP photoreaction of *t*-4BrS was investigated in 1,4-dioxane-d_8. The mass spectrometry showed 100% incorporation of deuterium in *t*-S produced. Whereas formation of *t*-S was also observed for the NRTP reaction of *t*-4BrS in hexane, the pathway was less significant than in 1,4-dioxane, probably due to the lower efficiency of hexane as a hydrogen source. A possible intervention of a polar reactive intermediate like *t*-stilben-4-yl cation would be excluded, since the NRTP photoreactions of *t*-4BrS in methanol and ethanol does not yield the corresponding alkoxy substituted stilbene at all.[9]

Although the electronic nature of the two-photon allowed excited state (A_g symmetry) of *t*-S has not yet been depicted in detail,[2e] the observed homolytic C-Br bond fission *via* NRTP excitation of *t*-4BrS may suggest the nonionic biradicaloid nature of the excited state. Further works will be needed to obtain a reasonable picture of the two-photon allowed excited states of stilbenes.

References and Note

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9 If the reaction occurs from a higher triplet excited state formed *via* a consecutive two-photon excitation such as S→T and T→T', as suggested by a referee, the formation efficiency should be independent of the polarization of the incident light in solution.[5a] The polarization ratio, which is defined as the ratio of the formation efficiency for the circularly polarized light to that for the linearly polarized light, was found to be about 0.7 for the NRTP photoreaction of *t*-4BrS. The ratio is good in accord with the polarization ratio obtained for the two-photon absorption spectrum (0.6), being indicative of the NRTP nature of the reaction.

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