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Remarkable Suppression of [2+2] Cycloaddition during Nonresonant Two-photon Photoreaction of *trans*-Stilbene in the Presence of Tetramethylethylene*

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ABSTRACT

Nonresonant two-photon excitation of *trans*-stilbene in the presence of an excess amount of tetramethylethylene induced predominantly *cis–trans* isomerization; the [2+2] intermolecular cycloaddition pathway was remarkably suppressed, in contrast to the one-photon excitation under similar conditions, where the cycloaddition is known to be the major pathway.

INTRODUCTION

Whereas a number of organic photoreactions in solution have been investigated in relation to their synthetic utility, design for optoelectronic devices and understanding the mechanism for eyesight, most studies have dealt with the events after one-photon excitation of molecules. Because the direct excitation to a two-photon-allowed excited state is achieved by applying nonresonant two-photon (NRTP)† excitation using a short-pulsed laser with high peak intensity as first predicted by Göppert-Mayer (1), the NRTP method may provide a new tool for the selective photoreactions of organic molecules. We have recently reported highly selective organic and organometallic photoreactions using NRTP excitation under ambient conditions (2–4). Typically, the NRTP excitation of *cis*-stilbene (*c*-S) using 532 nm laser pulses caused only isomerization to *trans*-stilbene (*t*-S) in hexane at room temperature lacking the cyclization to dihydrophenanthrene (DHP), which is usually a major side reaction during common one-photon excitation of *c*-S; for reviews, see Saltiel and Charlton (5), Waldeck (6), Allen and Whitten (7), and Hudson and Kohler (8). The NRTP method holds great promise as a new technique not only for controlling photochemical reaction pathways in condensed systems at ambient temperatures but also for elucidation of the mechanistic details. The NRTP study suggests that an excited state with A symmetry (a two-photon-allowed state) of *c*-S is responsible for the isomerization to *t*-S, while the excited state responsible for the cyclization to DHP may be the lowest singlet state with B symmetry. The action spectra of the NRTP isomerization from *t*-S to *c*-S show the maximum at 474 nm (4) and the spectral feature is in good agreement with the two-photon spectra of *t*-S reported by Stachelek *et al.* (9), Fuke *et al.* (10) and Hohlneicher and Dick (11). The results are well explained by the Hohlneicher and Dick model (11), in which some details of the Orlandi and Siebrand model (12) are modified and the 4A state rather than 2A state correlates with the lowest excited state at the perpendicular geometry of stilbene.

Herein, we have found that the NRTP reaction of *t*-S in the presence of tetramethylethylene (TME) showed predominantly *cis–trans* isomerization with significant suppression of the intermolecular [2+2] cycloaddition between *t*-S and TME, in contrast to the results of the one-photon irradiation of *t*-S, where predominant formation of *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (CB) is observed by Chapman and coworkers (13,14) and Saltiel *et al.* (15). Whereas the cycloaddition is often considered to involve an exciplex between the lowest singlet excited state of *t*-S and TME as an intermediate, Peters *et al.* (16) have recently shown that there is no kinetic evidence for reversible exciplex formation and if an exciplex does exist, its lifetime must be less than 10 ps. The present NRTP results may give direct evidence that the photochemical intermolecular [2+2] cycloaddition takes place from the lowest singlet excited state of *t*-S (B_u symmetry), while the isomerization of *t*-S to *c*-S occurs from the two-photon-allowed excited state (A_g symmetry).

MATERIALS AND METHODS

Trans-stilbene (Wako) was purified by recrystallization from ethanol. Tetramethylethylene (Tokyo Kasei) and spectrograde hexane

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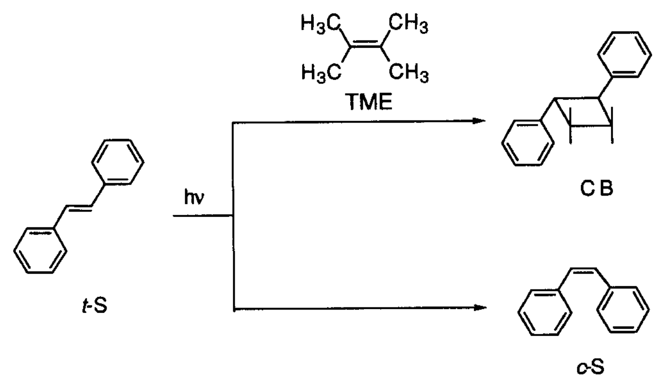
†*Abbreviations:* CB, *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane; DHP, dihydrophenanthrene; GC, gas chromatography; NRTP, nonresonant two-photon; TME, tetramethylethylene.



Scheme 1.

(Uvasol, Kanto) were used as received. The photoreactions were carried out in a quartz cell (GL Science; the optical width, 4 mm; the optical length, 10 mm) under irradiation of the 532 nm (6 ns pulsewidth; 100 mJ/pulse) and 266 nm (*ca* 5 ns pulsewidth; 2.5 mJ/pulse) laser pulses that were generated by a pulsed (10 Hz) Nd: YAG laser with a harmonic generator and a separator (Spectra Physics, GCR 250-10). A capillary gas chromatograph (GC, Shimadzu 14 AH) and a mass spectrometer (Hewlett Packard, 5971 A) with a capillary GC (HP 5890) were used for analysis of the product distribution. Decane was added as an internal standard for determining chemical yields of products.

RESULTS AND DISCUSSION

In accordance with the previous studies of one-photon photoreactions of *t*-S in the presence of TME (13–15), irradiation of a hexane solution of *t*-S ($1.7 \times 10^{-2}\,M$) in the presence of 4.0 *M* of TME at room temperature with a 266 nm laser light for 33 min gave CB, *c*-S and *t*-S, in 77, 5 and 5% yields, respectively, as determined by GC; no other volatile product was detected by GC. Dependence of the product distribution on irradiation time is shown in Fig. 1a.

Quite different results were obtained when *t*-S was irradiated in the presence of TME with 532 nm laser light at room temperature. Thus, irradiation of a hexane solution of *t*-S ($1.7 \times 10^{-2}\,M$) in the presence of TME (4.0 *M*) with the 532 nm laser induced predominantly *cis–trans* isomerization with remarkable suppression of the formation of CB as shown in Fig. 1b. After irradiation for 195 min, the absolute yields of CB, *c*-S and *t*-S were 5, 50 and 45%, respectively. It was confirmed that CB is intact upon irradiation with 532 nm laser light for >200 min. Similar to the *cis–trans* isomerization of stilbenes in the absence of TME, the yield of *c*-S after correction for the backward reaction from *c*-S to *t*-S with Lamola's equation (17) increased in proportion to the square of the incident laser intensity as shown in Fig. 2. As expected, the initial product ratio, $[\mathrm{CB}]_0/[c\text{-S}]_0$, depended on the initial concentration of TME, $[\mathrm{TME}]_0$. However, the ratios divided by $[\mathrm{TME}]_0$, $[\mathrm{CB}]_0/\{[c\text{-S}]_0[\mathrm{TME}]_0$, were almost constant for both the one-photon and two-photon reactions with the values of 0.7 and 0.023 M^{-1}, respectively; the large difference of the reaction selectivity between one-photon and NRTP excitation is quite remarkable. Because a recent picosecond kinetic study by Peters *et al.* (16) of the photocycloaddition of *t*-S with TME has shown that the cycloaddition occurs concertedly between the lowest excited state (B_u) and TME without forming an exciplex, the observed

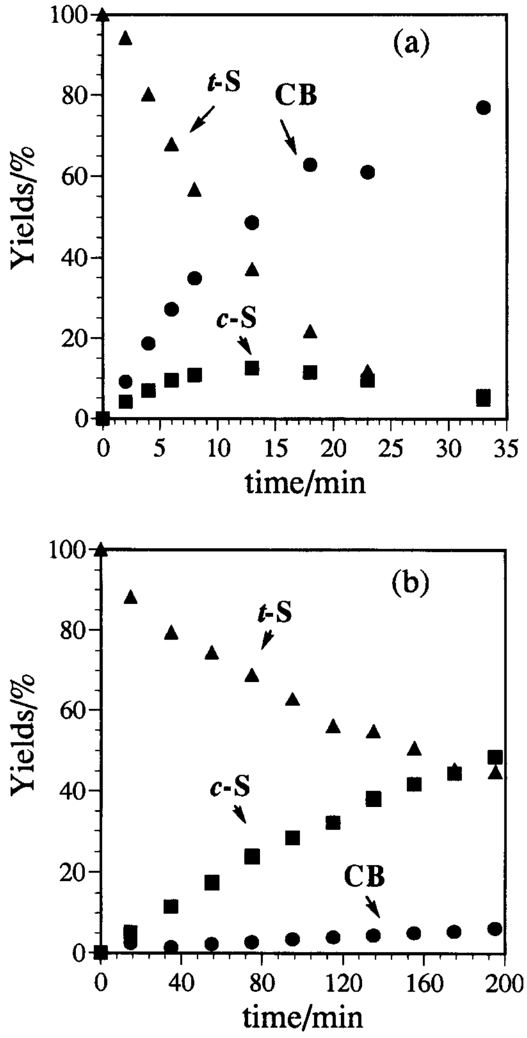


Figure 1. Time profile of the product distribution (*t*-S, *c*-S and CB) during irradiation of *t*-S with (a) 266 nm and (b) 532 nm in the presence of TME (4.0 *M*).

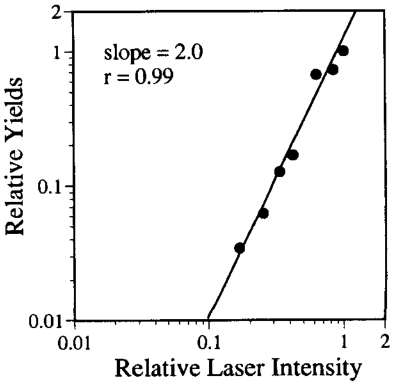


Figure 2. A representative plot of the relative yields of *c*-S after correction for the backward reaction *versus* the incident laser intensity for the isomerization of *t*-S using 532 nm laser pulses with the linear polarization.

selectivity should not originate from the secondary photolysis of the exciplex.

The origin of the selectivity would be ascribed to the difference of the selection rule between the one-photon and the NRTP excitation. Thus, the [2+2] cycloaddition will take place from the lowest singlet (B_u) excited state of *t*-S, while the isomerization to *c*-S will occur from the two-photon-allowed A_g state. If the A_g state is assumed to have a steep downhill potential surface from the planar Frank–Condon geometry to the energy minimum at the perpendicular geometry, the present results may suggest that the rotation around the central bond in the A_g state may compete with or be even more rapid than the internal conversion to the B_u at the planar *t*-S structure, in violation of Kasha's rule (18).

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