

Intramolecular photocycloaddition of β -stilbazoles tethered by silyl chains

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Received 31 July 2006; revised 2 September 2006; accepted 5 September 2006
Available online 26 September 2006

Abstract—Intramolecular (2+2) photocycloaddition of β -stilbazoles tethered by silyl chains took place with high efficiency. Complexation with dicarboxylic acid or catechol further enhanced both the efficiency and stereoselectivity.
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The photophysical properties and photochemical reactions of stilbazoles and stilbazolium salts have been extensively studied, and three types of photochemical reaction of these compounds are known: (1) photodimerization,^{1–8} (2) cis–trans photoisomerization,⁹ and (3) photocyclization to azaphenanthrenes via oxidative dehydrogenation in the presence of oxidants.¹⁰ Among them, intermolecular photodimerization of stilbazoles proceeds only slowly in homogeneous organic solutions, even at high concentrations. The intermolecular photodimerization of α -, β -, and γ -stilbazoles has reportedly been enabled by photoirradiation in solid state,¹ micelles,^{1c,2} cyclodextrins,³ clays,⁴ zeolite cages,⁵ Nafion membranes,⁶ polymer films,⁷ and aqueous solutions with acid or templates.⁸ These results may indicate that an appropriate distance between two stilbazole double bonds is necessary for their photodimerization. However, even under these circumstances, it is often difficult to control regioselectivity, and mixtures of both head-to-head and head-to-tail photodimers are produced. Recently, we reported three similar types of photochemical reaction in stilbenes, and found that they can be effectively controlled by tethering two stilbene units using silyl chains.¹¹ In the study presented here, we examined the synthesis and photoreactions of silyl-tethered stilbazoles.¹² In particular, to increase the efficiency, regioselectivity, and stereoselectivity for the photocycloaddition of stilbazoles, we investigated the effects of

distance between two double bonds and those of external additives.

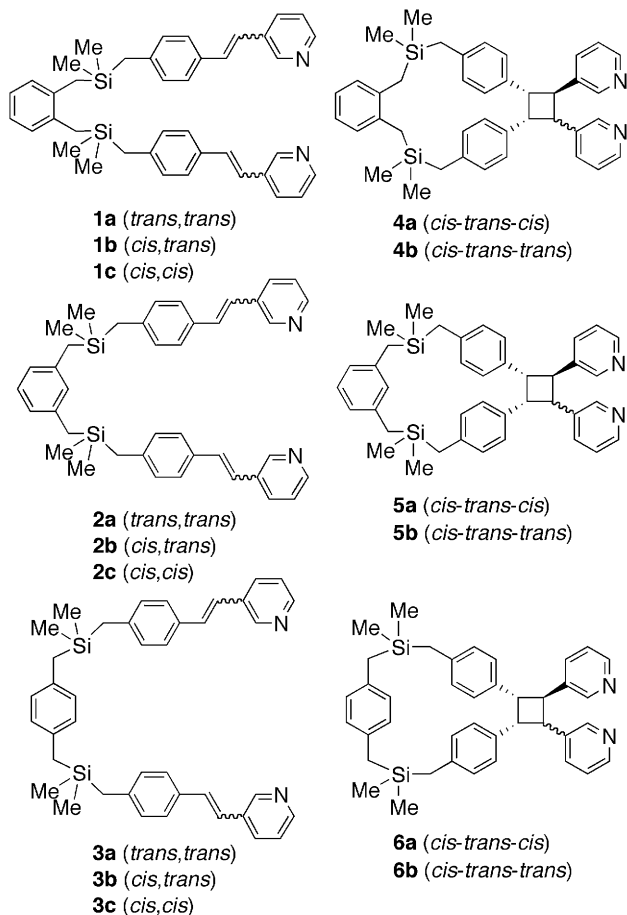
Silyl-tethered stilbazole derivatives **1–3** were designed and synthesized as candidates with appropriate distances between two stilbazole units (Scheme 1). We chose silyl chains because it has often been reported that the intersystem crossing of organosilicon compounds in the excited state is relatively slow,^{11,13} and selective generation of excited singlet and triplet states is expected. Moreover, silyl tethers can be removed after the event.

Synthesis of **1a**, **2a**, and **3a** are shown in Scheme 2. Grignard reaction of *ortho*-, *meta*-, and *para*-xylylene dichlorides **7a–c** with chlorodimethylsilane gave hydrosilanes **8a–c**, which were converted to chlorosilanes **9a–c** by PdCl₂ and CCl₄. Chlorosilanes **9a–c** were then allowed to react with Mg and *p*-vinylbenzyl chloride to give **10a–c**. Finally, Heck reaction¹⁴ of **10a–c** with 3-iodopyridine gave stilbazole derivatives **1a**, **2a**, and **3a**. Spectral data were in good agreement with these structures.¹⁵ The UV absorption maxima of silylmethyl substituted stilbazoles were shifted to longer wavelengths than that of unsubstituted β -stilbazole.¹⁶ Although the fluorescence of stilbazoles is very weak,¹⁷ the fluorescence intensity increased following the introduction of the silyl substituents.^{11,13}

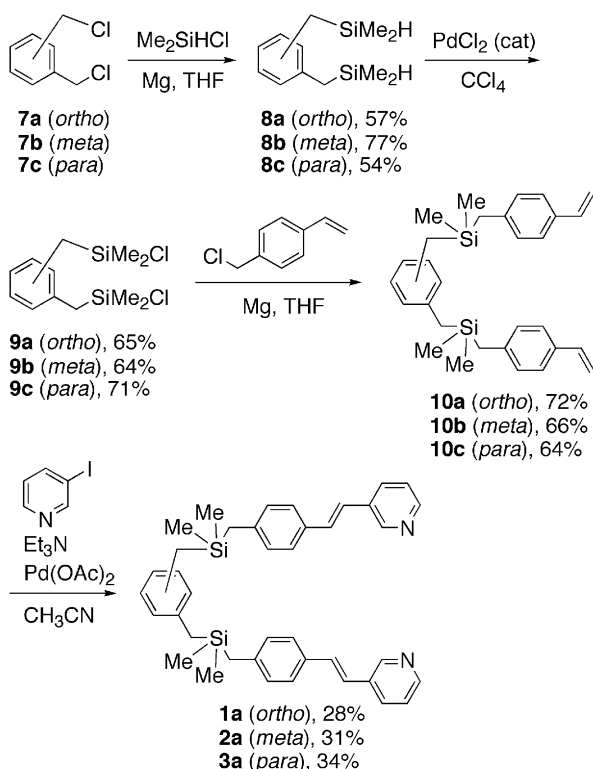
Cis–trans photoisomerization and intramolecular photocycloaddition competitively proceeded upon photoirradiation of a degassed benzene-*d*₆ solution containing *ortho*-*trans*,*trans* derivative **1a** (0.02 M), using a Xenon lamp through a Pyrex filter (>280 nm). Time

Keywords: Intramolecular photocycloaddition; β -Stilbazole; Stilbazolium; Silyl chain; Dicarboxylic acid.

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Scheme 1. Silyl-tethered stilbazoles and their photocycloadducts.



Scheme 2. Synthesis of silyl-tethered stilbazoles.

dependency of the photoreaction is shown in Figure 1a. Photoirradiation of the solution of **1a** caused *cis*–*trans* photoisomerization and gave the *cis,trans* isomer **1b** first, before the *cis,cis* isomer **1c**. Prolonged photoirradiation of the solution containing the stereoisomers **1a**–**c** resulted in the formation of intramolecular photocycloadducts **4a** and **4b** with stereochemistry *cis*–*trans*–*cis* and *cis*–*trans*–*trans*, respectively, suggesting that **4a** and **4b** were formed through the photocycloaddition of **1a** and **1b**, respectively, via an excited singlet.

Photoreactions of *meta*- and *para*-substituted derivatives **2a** and **3a** proceeded via a similar sequence (Fig. 1b and c), with the rates for the intramolecular photocycloaddition decreasing in the order of **1a** (*ortho*) > **2a** (*meta*) > **3a** (*para*). These data indicate that the rate for the photocycloaddition increases with decreasing distance between the two double bonds. As noted above, the intermolecular photocycloaddition of stilbazoles in organic solutions is not an efficient process. Indeed, when we attempted the photoreaction of counterpart **11a** under conditions identical to those described above for 24 h (Scheme 3), the *cis*–*trans* photoisomerization took place with a photostationary state ratio of **11a**:**11b** = 3:7, without the formation of head-to-head and head-to-tail intermolecular photodimers in detectable amounts.

Further increase of the efficiency and stereoselectivity in the photocycloaddition should be attained by two pyridyl groups using external additives. After several rounds of trial and error, we found that a methanol reflux of an equimolar mixture of **2a** and *cis*-1,2-cyclohexanedicarboxylic acid for 6 h gave macrocyclic stilbazolium carboxylate **12a** in 76% yield as a colorless solid (mp 183–191 °C) (Scheme 4). Treatment of a benzene solution containing **12a** with aqueous NaHCO₃ solution and a following work-up reproduced **2a** (mp 128–130 °C).

Comparing the photoreaction of **12a** with that of the uncomplexed molecule **2a**, the rate for the photocycloaddition increased. Moreover, we obtained a single stereoisomer of the photocycloadduct **13** (Fig. 1d). We propose that these effects may be attributable to the shorter distance between the two double bonds and/or the conformational restriction specific to the cyclized compounds. Indeed, the photoreaction of compound **14** in which two stilbazoles were connected by the dimethylsilyl tether and catechol¹⁸ predominantly produced the intramolecular photocycloadduct **15** stereoselectively by only 6 h of irradiation (Scheme 5).

When benzene solutions of **2a** and **12a** were irradiated (>360 nm) in the presence of pyrene (2 equiv) as a triplet photosensitizer, it caused only *cis*–*trans* photoisomerization and gave photostationary state mixtures of **2a**–**c** and **12a**–**c** in **2a**:**2b**:**2c** = 14:33:53 and **12a**:**12b**:**12c** = 14:46:40 ratios within 10 h of irradiation, respectively. The lower ratio of **12c** compared to the ratio of **2c** suggests that some rigidity might be involved in **12**.

From these results, we propose that intramolecular photocycloaddition of these compounds proceeds via

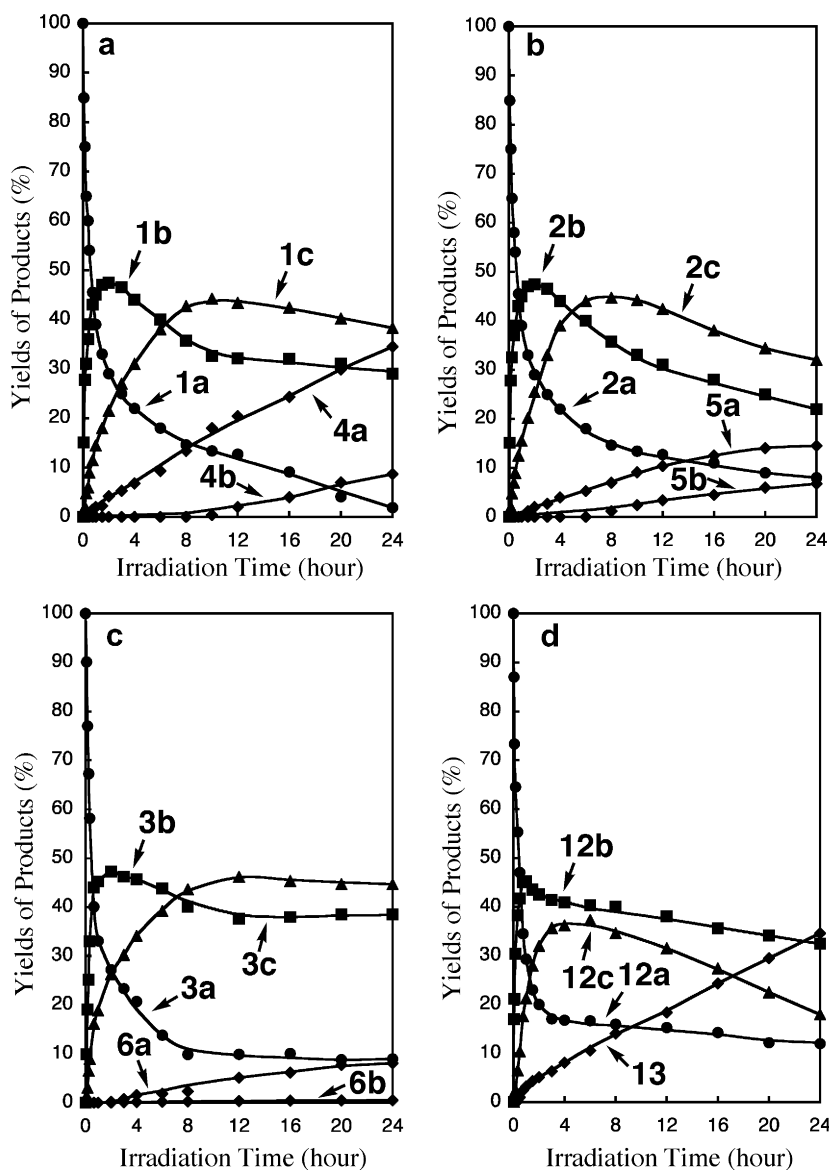
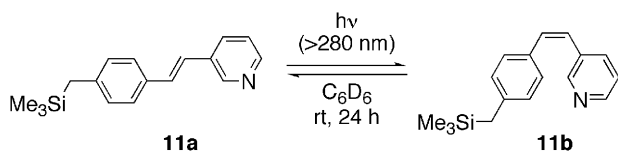


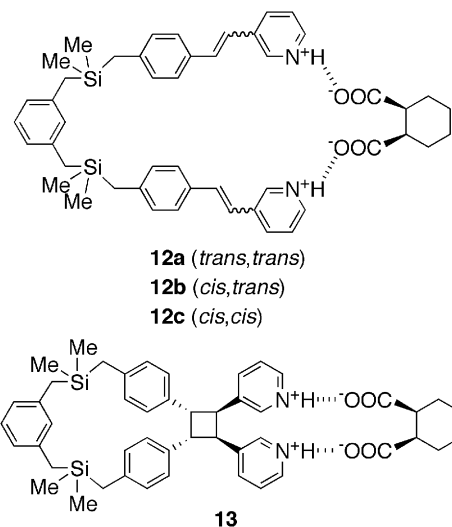
Figure 1. Time dependency in photoreaction of (a) 1a, (b) 2a, (c) 3a, and (d) 12a in benzene-*d*₆. [1a]₀ = [2a]₀ = [3a]₀ = [12a]₀ = 0.02 M.



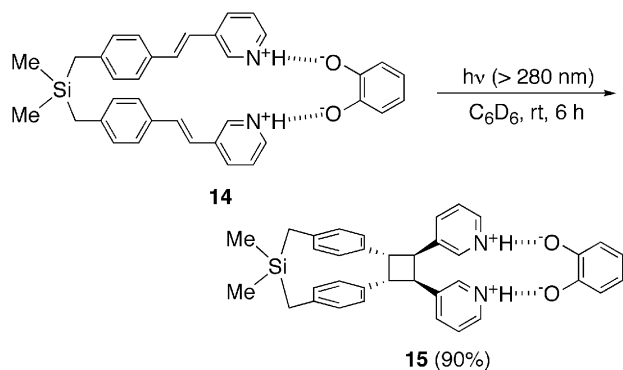
Scheme 3.

excited singlet. The efficiency of the intramolecular photocycloaddition depends on the distance between two double bonds and appropriate geometry. Cis–trans photoisomerization occurs via involving both excited singlet and triplet states. Silyl tethers contribute to suppression of intersystem crossing from excited singlet to excited triplet.

In conclusion, the efficiency, regioselectivity, and stereoselectivity of photodimerization of stilbazolium were dramatically enhanced by tethering two stilbazolium



Scheme 4. Macrocyclic stilbazolium and its photocycloadduct.



Scheme 5.

intramolecularly with silyl chains. The complexation of these compounds with dicarboxylic acid or catechol further enhanced both the efficiency and stereoselectivity of the photocycloaddition.

Acknowledgements

This work was supported by the Corporation of Innovative Technology and Advanced Research in Evolutional Area (CITY AREA) from the Wakayama Technology Promotion Foundation. This work was also supported by a Grant-in-Aid for Scientific Research (KAKENHI) on Priority Areas ‘Molecular Nano Dynamics’ (17034056), ‘Advanced Molecular Transformations of Carbon Resources’ (18037063), and Young Scientists (B) (16750039) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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- Data for **1a**: mp 219–220 °C; ¹H NMR (300 MHz, CDCl₃): δ -0.08 (s, 12H), 1.93 (s, 4H), 2.11 (s, 4H), 6.87–7.01 (m, 10H), 7.10 (d, *J* = 16.5 Hz, 2H), 7.22–7.27 (m, 2H), 7.38 (d, *J* = 8.2 Hz, 4H), 7.77 (dt, *J* = 8.1, 1.5 Hz, 2H), 8.45 (dd, *J* = 4.7, 1.5 Hz, 2H), 8.68 (d, *J* = 2.0 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ -3.24, 22.34, 26.00, 123.04, 123.33, 124.01, 126.44, 128.32, 128.80, 130.58, 132.30, 132.38, 133.06, 136.06, 140.32, 147.77, 147.95. Data for **3a**: mp 139–140 °C; ¹H NMR (300 MHz,

- CDCl₃): δ -0.05 (s, 12H), 2.06 (s, 4H), 2.12 (s, 4H), 6.85 (s, 4H), 6.97 (d, J = 8.0 Hz, 4H), 6.98 (d, J = 15.9 Hz, 2H), 7.12 (d, J = 16.1 Hz, 2H), 7.24–7.29 (m, 2H), 7.38 (d, J = 8.0 Hz, 4H), 7.80 (d, J = 8.2 Hz, 2H), 8.45 (d, J = 4.9 Hz, 2H), 8.69 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ -3.49, 24.60, 25.48, 123.02, 123.32, 126.41, 127.89, 128.35, 130.62, 132.23, 132.33, 133.08, 134.85, 140.44, 147.89, 148.08.
16. Data for **1a**: λ_{\max} = 320 nm, ϵ = 6.2×10^4 mol⁻¹ dm³ cm⁻¹. Data for **11a**: λ_{\max} = 320 nm, ϵ = 2.4×10^4 mol⁻¹ dm³ cm⁻¹. Data for 2-(2-(*p*-tolyl)vinyl)pyridine: λ_{\max} = 311 nm, ϵ = 1.7×10^4 mol⁻¹ dm³ cm⁻¹. All data were obtained in CH₂Cl₂ at 298 K.
17. Φ_f (β -stilbazole) = 0.064 in 3-methylpentane at 296 K. See: Barigelletti, F.; Dellonte, S.; Orlandi, G.; Bartocci, G.; Masetti, F.; Mazzucato, U. *J. Chem. Soc., Faraday Trans. I* **1984**, *80*, 1123–1129. See also Ref. 9b.
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