Intramolecular ($2\pi + 2\pi$) Photocycloaddition of Styrenes Tethered by Siloxanes

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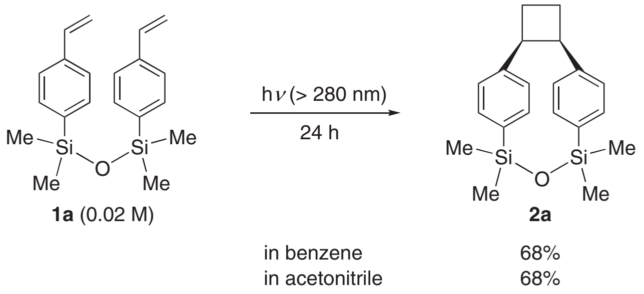
Intramolecular ($2\pi + 2\pi$) photocycloaddition of styrenes tethered by flexible siloxane chains gave the corresponding cyclobutacyclophanes in high yields. Triplet-sensitization was found to be effective for the photocycloaddition.

Inter- and intramolecular photocycloaddition of two chromophores is a useful strategy for the preparation of various organic molecules.[1] Silyl chains and silyl groups play peculiar roles in photocycloaddition, i.e., they provide bulkiness and some kind of rigidity, interact with heteroatom substituents, lower the oxidation potentials, etc.[2] Intramolecular photocycloaddition of styrenes is of particular importance for the synthesis of cyclophanes including cyclobutane rings.[3] To the best of our knowledge, there are only a few papers for the intramolecular photocycloaddition of styrenes tethered by silyl chains. Those are intramolecular photocycloaddition of bis(cinnamyloxy)silanes[4] and bis(*p*-vinylphenylmethyl)silanes.[5] With the aim to develop more flexible covalent silyl tethers bridging two chromophores, we have investigated here the intramolecular photocycloaddition of styrenes tethered by disiloxanes.



Scheme 1.

Photoirradiation of a benzene solution containing 1,1,3,3-tetramethyl-1,3-bis(*p*-vinylphenyl)disiloxane (**1a**) by a high-pressure Hg lamp through Pyrex filter under argon atmosphere for 24 h gave an intramolecular *cis*-fused photocycloadduct **2a** as the only product in a 68% isolated yield.[6] The photocycloaddition also proceeded in CH_3CN solution. IR absorption spectrum of **2a** showed intense peak at 1035 cm^{-1}, ascribable to the Si–O–Si stretching mode, but failed to show a peak assigned to SiO–H stretching mode. Therefore, it was concluded that the Si–O–Si linkage of the product was not cleaved. ^1H NMR spectrum of **1a** in $CDCl_3$ at room temperature showed one pair of aromatic AB quartet, but that of **2a** showed two pairs of aromatic AB quartet. These results indicate that the two benzene rings of **2a** cannot be rotated.

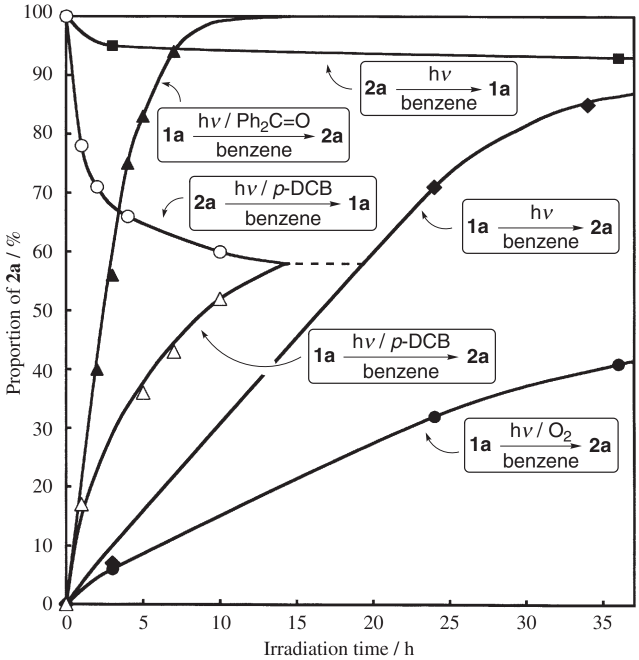
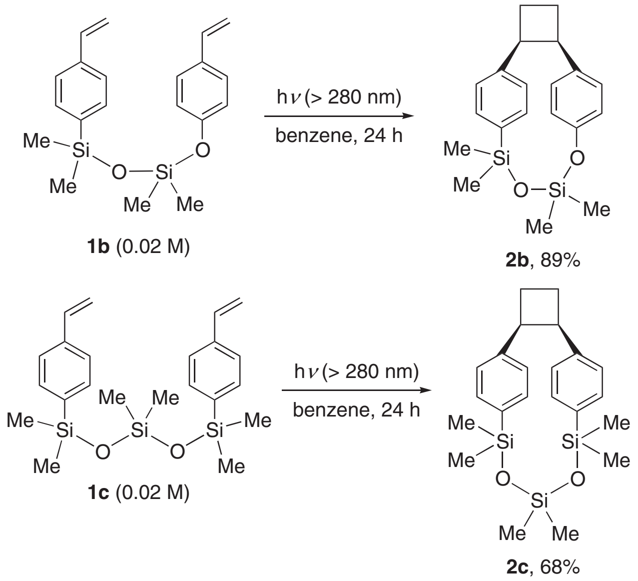


Figure 1. Effects of additives in photocycloaddition and photocycloreversion of **1a**/**2a**.



Scheme 2.

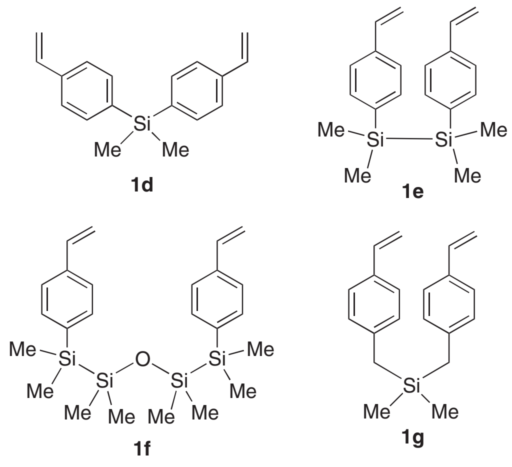
Next we have examined the effect of additives and reversibility in the photoreaction of **1a**.[7] Photoirradiation of a benzene solution of **1a** and that of **2a** gave a photostationary state (PSS) mixture (**1a**:**2a** = 1:9) by prolonged irradiation. The addition of two equivalents of benzophenone accelerated the reaction. Photoreaction of **2a** in the presence of benzophenone did not afford detectable amount of **1a**. Photoreaction of **1a** under saturated O_2 proceeded more slowly than the reaction in the absence of O_2.

Addition of equimolar amount of *p*-dicyanobenzene (*p*-DCB) as an electron-transfer photosensitizer accelerated both photocycloaddition and photocycloreversion, whose PSS ratio of **1a**:**2a** was estimated to be 4:6.

Photocycloaddition of styrenes with longer siloxane chains **1b** and **1c** gave also the corresponding intramolecular photocycloadducts **2b** and **2c** in good yields, respectively. ^{1}H NMR spectra of **2b** and **2c** showed four and two pairs of AB quartet, respectively. These results indicate that the two benzene rings of **2b** and **2c** also cannot be rotated. Photoreaction of silane **1d** under the same reaction conditions resulted in almost recovery of **1d**. Photoirradiation of disilanes **1e** and **1f** gave polymerized products, although photoreaction of **1g** proceeded efficiently as previously reported.[5]

Fluorescence spectra of **1a–e** and **1g** were measured in aerated cyclohexane ($[\mathbf{1}] = 1.0 \times 10^{-4}$ M, $\lambda_{ex} = 287$ nm). Monomer emission of **1a–c** was efficiently quenched intramolecularly as compared to that of **1d**. Fluorescence of disilane **1e** appeared at a longer wavelength than those of **1a–d** and **1g**.[8]

From these results, we have concluded that the photocycloaddition and photocycloreversion occur via involving both excited singlet and triplet states. In direct photoirradiation, the reaction proceeds via a non-emissive intramolecular singlet excimer. In the triplet-sensitized photoreaction, the reaction proceeds through the excited triplet state. *p*-DCB-sensitized photoreaction occurs by an electron-transfer mechanism via their radical cations producing different ratio of products.[5b]



Scheme 3.

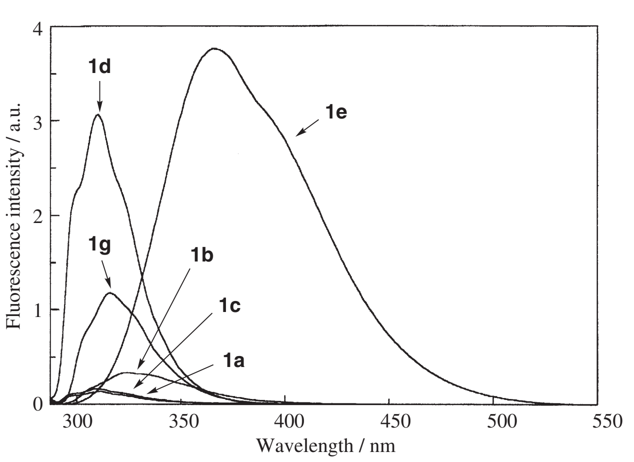


Figure 2. Fluorescence spectra of **1a–e** and **1g** in cyclohexane ($[\mathbf{1}] = 1.0 \times 10^{-4}$ M, $\lambda_{ex} = 287$ nm).

In conclusion, we have developed efficient intramolecular photocycloaddition of styrenes tethered by siloxane chains as flexible silyl chains.

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References and Notes

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6 **Data for 2a**: mp 152–153 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.34 (s, 6H), 0.36 (s, 6H), 2.50–2.56 (m, 4H), 4.12–4.18 (m, 2H), 6.39 (dd, $J = 7.6$, 1.5 Hz, 2H), 6.78 (dd, $J = 7.6$, 1.5 Hz, 2H), 6.86 (dd, $J = 7.6$, 1.5 Hz, 2H), 6.99 (dd, $J = 7.6$, 1.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.73, 20.33, 47.23, 126.22, 130.11, 133.03, 133.14, 135.59, 142.32; IR (KBr) 2954, 1908, 1592, 1392, 1250, 1197, 1113, 1035, 836, 790, 724 cm^{-1}; MS (EI) m/z (%) = 193 (52), 219 (100), 323 (17), 338 (M^+, 25).

7 Formation of polymeric products derived from polymerization of styrene was negligible under these reaction conditions shown in Figure 1. Prolonged irradiation gave insoluble polymers, especially in the *p*-DCB-sensitized photoreaction.

8 This phenomenon is due to the excitation of intramolecular charge transfer complex. See: a) H. Shizuka, Y. Sato, Y. Ueki, M. Ishikawa, and M. Kumada, *J. Chem. Soc., Faraday Trans. 1*, **80**, 341 (1984). b) H. Sakurai, *Pure Appl. Chem.*, **59**, 1637 (1987).

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