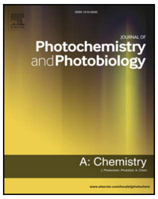
Journal of Photochemistry & Photobiology A: Chemistry 364 (2018) 472–477

Contents lists available at ScienceDirect

Journal of Photochemistry & Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Synthesis of silicon-containing macrocyclic compounds by using intramolecular [2 + 2] photocycloaddition reactions of bis-dimethylsilyl-linked styrenes and stilbenes

Hajime Maeda*, Ko-ichi Nishimura, Ryu-ichiro Hiranabe, Kazuhiko Mizuno**

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

ARTICLE INFO

Keywords:
Photocycloaddition
Macrocyclic compounds
Silicon
Styrene
Stilbene

ABSTRACT

A method for the synthesis of silicon-containing macrocyclic compounds, using intramolecular [2 + 2] photocycloaddition reactions of bis-dimethylsilyl-linked styrene or stilbene derivatives, is described. Photoirradiation of benzene solutions of *o*- and *m*-bis(dimethylsilylmethyl)benzene derivatives, containing two styrene units, promotes efficient formation of intramolecular [2 + 2] photocycloadducts. In contrast, photoreaction of the corresponding *para*-substituted analog generates only dimers. Photoreactions of bis(dimethylsilylmethyl)benzene derivatives, possessing two stilbene units produce intramolecular [2 + 2] photocycloadducts along with products of *cis-trans* photoisomerization. The efficiencies of these intramolecular photoreactions depend on the distances between two double bonds undergoing [2 + 2] cycloaddition. Triplet-sensitized photoreactions of the stilbene derivatives lead to *cis-trans* isomerization exclusively. Finally, photoreactions of the stilbene derivatives in the presence of molecular oxygen produce phenanthrene derivatives as side products.

1. Introduction

Intramolecular photocycloaddition reactions of styrenes and stilbenes have been extensively studied because they serve as useful methods for the synthesis of cyclic organic compounds [1–10]. We have also reported that intramolecular photocycloaddition reactions of styrenes and stilbenes tethered by silicon containing chains can be used to prepare cyclic compounds that possess silyl moieties within the rings [11–15]. Silicon-containing medium-size and macrocyclic compounds, prepared by using a variety of protocols, have attracted recent attention owing their structural properties and guest-inclusion abilities [16–26]. In the effort described below, intramolecular photocycloaddition reactions of bis-dimethylsilyl-linked styrenes and stilbenes were explored to demonstrate their use in the preparation of silicon-containing macrocyclic compounds.

2. Results and discussion

The bis(dimethylsilylmethyl)benzene derivatives containing two styrene or stilbene units, that are the focus of this study, were prepared employing the routes outlined in Scheme 1. In the pathways, Grignard reagents prepared from *o*-, *m*-, and *p*-xylylene dichloride **1a-c** react with chlorodimethylsilane to produce the respective hydrosilanes **2a-c**, which are chlorinated using $PdCl_2/CCl_4$ to form chlorosilanes **3a-c**. Magnesium promoted coupling reactions between **3a-c** and *p*-(chloromethyl)styrene produce the target substances bearing styrene units **4a-c**. Finally, Heck reactions of **4a-b** with iodobenzene generate the target substrates, ***trans*,*trans*-5a-b**, bearing *trans*-stilbene units.

UV absorption spectra of **4a-c** in 1.0×10^{-4} M CH_2Cl_2 solutions are displayed in Fig. 1. Absorption band of styrene (λ_{max} = 290 nm [27]) shifts to longer wavelengths region (λ_{max} = 300 nm) when silylmethyl groups are present on the benzene ring.

In the initial phase of this study, intramolecular photocycloaddition reaction of the *ortho* positioned bis-styrene containing substrate **4a** was explored. For this purpose, a benzene solution of **4a** (0.02 M) in a Pyrex vessel was degassed by using argon bubbling and then irradiated using a 300 W high pressure mercury lamp (> 280 nm) for 24 h. The crude photolysate was concentrated and subjected to silica gel column chromatography. This process led to isolation of the intramolecular [2 + 2] photocycloadduct **6a** in 36% yield (Scheme 2, Table 1, entry 1). The ^{1}H NMR spectrum of **6a** contains two multiplets centered at 2.42 ppm (4 H) and 3.93 ppm (2 H), which are assigned to methylene and methine

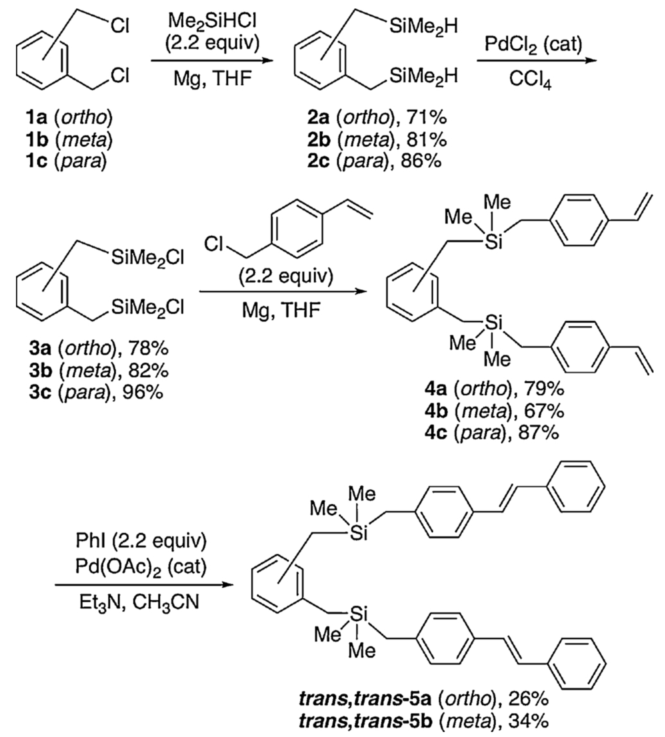
---

* Corresponding author. Present address: Division of Material Chemistry, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa, Ishikawa, 920-1192, Japan.

** Corresponding author. Present address: Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST), 8916-5 Takayama-cho, Ikoma, Nara, 630-0192, Japan.

E-mail addresses: maeda-h@se.kanazawa-u.ac.jp (H. Maeda), kmizuno@ms.naist.jp (K. Mizuno).

https://doi.org/10.1016/j.jphotochem.2018.06.038
Received 8 May 2018; Received in revised form 21 June 2018; Accepted 22 June 2018



Scheme 1. Preparation of bis(dimethylsilylmethyl)benzene derivatives containing two styrene or stilbene units.

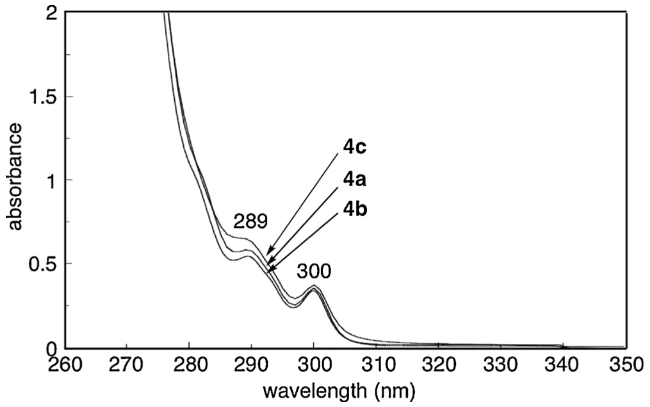
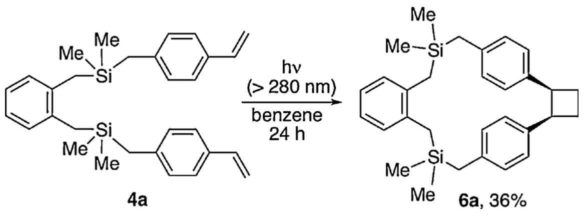


Fig. 1. UV absorption spectra of **4a-c** (1.0×10^{-4} M in CH_2Cl_2).



Scheme 2. Intramolecular photocycloaddition reaction of bis(dimethylsilylmethyl)benzene derivative **4a** containing two styrene units.

protons on the cyclobutane ring, respectively. In earlier studies of intramolecular photocycloaddition of styrenes, resonances of methine protons on *cis*-disposed 1,2-diarylcyclobutanes appear at 3.8–4.0 ppm in their ^{1}H NMR spectra, while those on *trans*-disposed 1,2-diarylcyclobutanes appear at upper fields as a consequence of the benzene ring current effect [2,5,6]. Based on these data, the stereochemistry on cyclobutane ring of **6a** is assigned to *cis*-orientation.

Table 1
Effect of photosensitizers on the photoreaction of **4a**.[a]

Entry	Solvent	Photosensitizer	Absorption of photosensitizer [b] (nm)	Isolated yield of **6a** (%)
1	Benzene	None	–	36
2	Benzene	1,4-Dicyanonaphthalene (0.25 equiv)	323 [32]	18
3	Benzene	Benzophenone (1 equiv)	344 [33]	Trace
4	Benzene	Michler's ketone (1 equiv)	580 [34]	Trace
5	Acetonitrile	*p*-Dicyanobenzene (0.25 equiv) + Phenanthrene (0.25 equiv)	346 [35]	Trace

[a] [**4a**] = 0.02 M, Pyrex vessel, irradiated by using a 300 W high pressure mercury lamp at rt for 24 h.

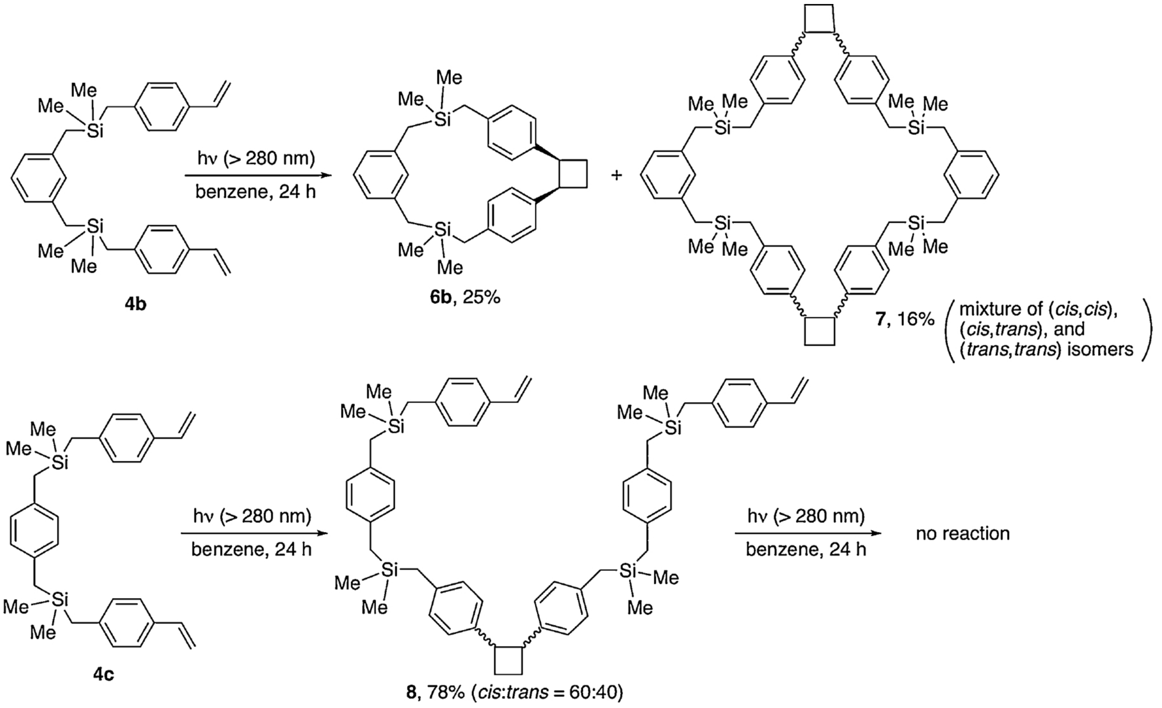
[b] Absorption maximum of photosensitizer at the longest wavelength.

The use of photosensitizers to promote reaction of **4a** was explored next. We observed that photoreaction of this substrate, carried out in the presence of 1,4-dicyanonaphthalene working as a single electron transfer (SET) or singlet triplex photosensitizer [12,28] generates, **6a** in a decreased 18% yield (Table 1, entry 2). Photoreactions of **4a**, promoted by using benzophenone or Michler's ketone as triplet energy transfer photosensitizers [11,13] (entries 3,4), or in the presence of *p*-dicyanobenzene and phenanthrene as SET photoredox sensitizers [29–31] (entry 5), produce **6a** in only negligible yields. The above results suggest that the ideal method for photocycloaddition reaction producing **6a** involves direct irradiation of **4a**.

Our attention next turned to photochemical studies with the *meta*- and *para*-substituted derivatives **4b** and **4c** (Scheme 3). Direct irradiation of a benzene solution of **4b** gave rise to formation of the intramolecular [2 + 2] photocycloadduct **6b** in 25% yield along with the [2 + 2] photodimer **7** in 16% yield. ^{1}H NMR spectroscopic analysis indicates that the stereochemistry of the cyclobutane ring in **6b** (3.94 ppm), like that in **6a**, is *cis*. In contrast, **7** is a mixture of (*cis*,*cis*), (*cis*,*trans*) and (*trans*,*trans*) stereoisomers, because methine protons on cyclobutane rings are observed at both 3.96–4.02 ppm (*cis*) and 2.82–2.93 ppm (*trans*). Photoreaction of the *para*-substituted derivative **4c** does not produce an intramolecular [2 + 2] photocycloadduct and only a mixture of stereoisomeric [2 + 2] photodimers **8** are formed in 78% yield, whose methine protons appear at 3.76 ppm (*cis*) and 3.14 ppm (*trans*). In order to determine if photocycloaddition reaction of the remaining two styrene units in **8** would take place, the isolated product was subjected to irradiation for 24 h. However, this substance remains unreacted under these conditions, likely a consequence of the spatially remote orientation of the two styrene units that prevents their interaction.

Next, light promoted reactions of ***trans,trans*-5a-b**, bearing two stilbene units, were conducted by using a Xenon lamp with a > 290 nm UV-29 cut filter (Scheme 4). Photoreactions take place under these conditions to generate mixtures of stereoisomeric pairs of respective intramolecular [2 + 2] photocycloadducts ***cis*,*trans*,*cis*-9a-b** and ***cis*,*cis*,*trans*-9a-b**, along with mixtures of the respective stereoisomeric products ***cis*,*trans*-5a-b** and ***cis*,*cis*-5a-b**. Unlike the photoreactions of **4b-c**, dimerized products were not observed. The stereochemistry of **9b** was determined by using ^{1}H NMR spectroscopy (Fig. 2). Based on molecular symmetry considerations and the observed up-field shift of cyclobutane ring methine protons by vicinal phenyl group, two doublet-like resonances at 4.33 (2 H) and 4.39 ppm (2 H) are assigned as *cis*,*trans*,*cis* stereoisomer. In a similar manner, four triplets (1H each) in the 3.64–4.02 ppm region in the ^{1}H NMR spectrum are assigned as *cis*,*cis*,*trans* stereoisomer.

The time dependencies of product distributions in photoreactions of ***trans*,*trans*-5a-b** in benzene-d_6 were monitored by using ^{1}H NMR spectroscopy (Figs. 3 and 4). The results show that at short irradiation times, *cis-trans* isomerization takes place on both substrates to form ***cis*,*trans*-5a-b** and ***cis*,*cis*-5a-b**. At longer irradiation times, [2 + 2]

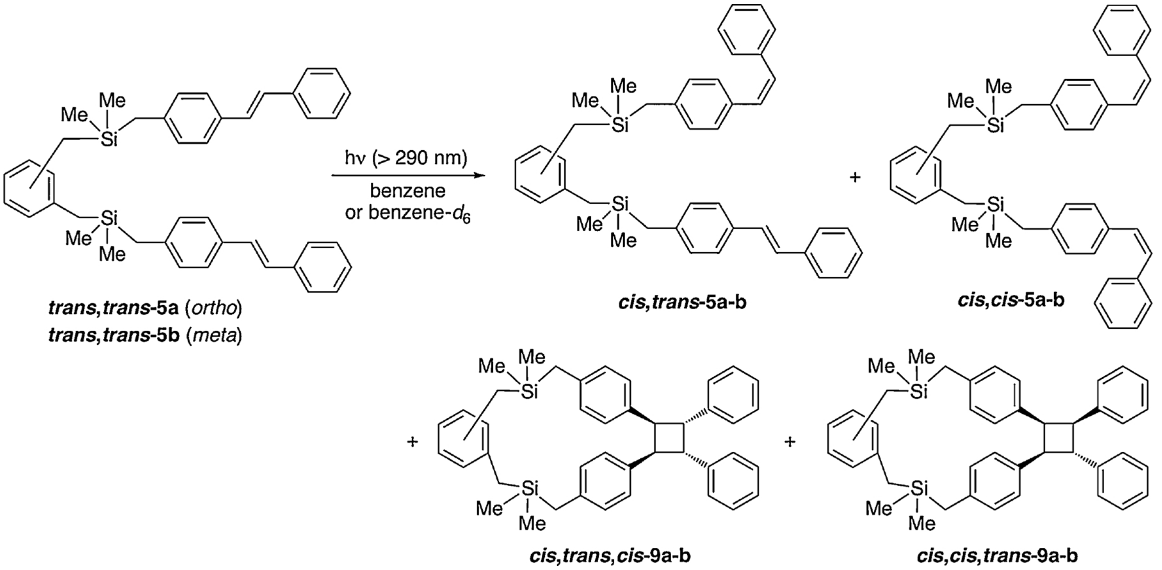


Scheme 3. Intramolecular [2 + 2] photocycloaddition reactions of bis(dimethylsilylmethyl)benzene derivatives **4b** and **4c** having two styrene units.

intramolecular photocycloadducts **9a-b** are then formed. We believe that the [2 + 2] cycloaddition processes occur via excited singlet states of the stilbene containing substrates with retention of double bond configuration. Thus, based on this assumption, ***cis,trans,cis*-9a-b** and ***cis*,*cis*,*trans*-9a-b** are produced by intramolecular [2 + 2] photocycloaddition of the respective ***trans*,*trans*-5a-b** and ***cis*, *trans*-5a-b** substrates. The observation that formation of ***cis*, *trans*, *cis*-9a-b** takes place faster than that of ***cis*, *cis*, *trans*-9a-b** and that the all-*cis* isomer is not generated appears to be a consequence of the higher reactivity of the *trans*-stilbene reactants over the *cis*-stilbene analogs [36]. In addition, the fact that photocycloaddition of *ortho* derivative **5a** giving **9a** proceeds faster than that of the *meta* derivative **5b** giving **9b** is likely a result of the higher efficiency of reactions of the substrate that possesses a shorter distance between the two double bonds.

To understand photochemical properties of the excited triplet states of the bis-stilbene containing substrates, triplet sensitization experiments were carried out. For this purpose, benzene-d_6 solutions of ***trans*,*trans*-5a-b** in the presence of 2 equiv of pyrene as a triplet photosensitizer were irradiated with > 360 nm light, and the progress of the reactions was monitored by using ^{1}H NMR spectroscopy (Scheme 5). The results show that intramolecular [2 + 2] photocycloadducts are not formed even after a 24 h irradiation period. However, *cis-trans* photoisomerization of the substrates occurs under these conditions to form respective photostationary state (PSS) mixtures of ***trans*,*trans*-5a-b**:***cis*,*trans*-5a-b**:***cis*,*cis*-5a-b** in 1:3:6 ratios. Thus, *cis-trans* isomerization is the only pathway followed in photoreactions of the excited triplet states of these substances [37,38], generated by energy transfer from the triplet excited state of pyrene (E_T = 48 kcal/mol [39]) to the mono-substituted stilbenes (E_T = 45–49 kcal/mol [40,41]).

The effects of molecular oxygen on these photoreactions were



Scheme 4. Intramolecular [2 + 2] photocycloaddition reactions of bis(dimethylsilylmethyl)benzene derivatives ***trans*,*trans*-5a-b** having two stilbene units.

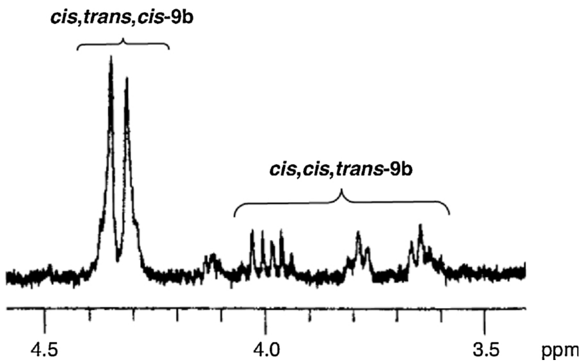


Fig. 2. ^{1}H NMR (300 MHz) spectrum of a mixture of ***cis,trans,cis*-9b** and ***cis,cis,trans*-9b** in $CDCl_3$.

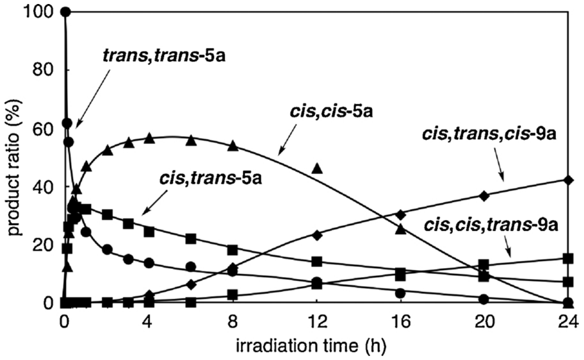


Fig. 3. Time-dependency of product distributions in photoreaction of ***trans,trans*-5a** in benzene-d_6 ([***trans,trans*-5a**]$_0$ = 0.02 M).

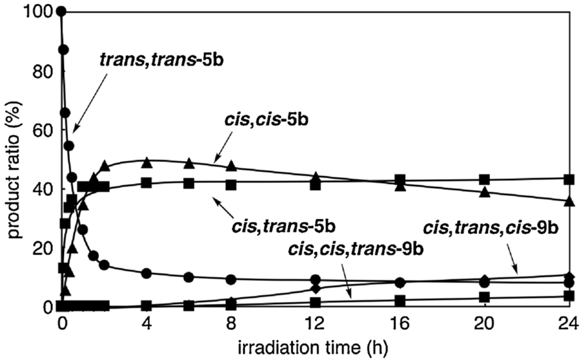
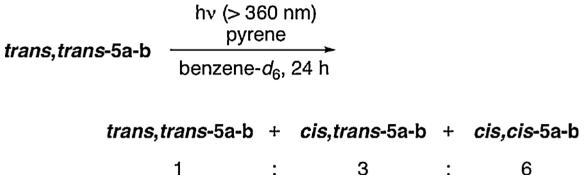
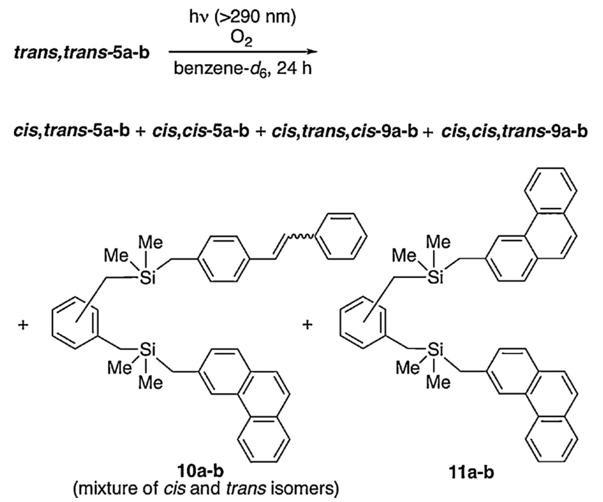


Fig. 4. Time-dependency of product distributions in photoreaction of ***trans,trans*-5b** in benzene-d_6 ([***trans,trans*-5b**]$_0$ = 0.02 M).



Scheme 5. Pyrene-sensitized *cis-trans* photoisomerization of **5a-b**.

explored next. We observed that irradiation of O_2-purged benzene-d_6 solutions of ***trans,trans*-5a-b** with > 290 nm light promotes formation of not only mixtures of stereoisomers of the reactants and intramolecular [2 + 2] photocycloadducts, but also mixtures of phenanthrene ring containing products (Scheme 6). Evidence for the existence of phenanthrene products in the mixtures comes from the observation of resonances at 8.5–9.0 ppm in ^{1}H NMR spectra of the crude photolysates, which are ascribable to H-4 and H-5 hydrogens on the phenanthrene ring. Although the phenanthrene ring containing products were not separated and characterized, it is likely that they have structures represented by **10a-b** and **11a-b** and that they arise by a photoelectrocyclization-oxidation pathway [42]. Formation of phenanthrene products in the photoreaction of **5b** (*meta*) was faster than that of **5a** (*ortho*). Since photocyclization to phenanthrene competes with photocycloaddition, **5a** has higher reaction rate of photocycloaddition than **5b**, instead, **5a** has lower reaction rate of photocyclization to give phenanthrene derivatives.



Scheme 6. Photoreactions of ***trans,trans*-5a-b** in the presence of dioxygen.

Analysis of the UV absorption and fluorescence spectra of ***trans,trans*-5a-b** (2.0×10^{-5} M in CH_2Cl_2, Figs. 5 and 6) show that their spectral characteristics are similar to those of *trans*-stilbene. Although the absorption and fluorescence maxima of ***trans,trans*-5a-b** are shifted to longer wavelengths by respective 10–11 and 19 nm as compared to those of *trans*-stilbene, the photochemical properties of these substrates are associated with free stilbene chromophores. Therefore, there is no need to consider that energy and electron transfer processes with bis(silylmethyl)benzene chains are involved.

3. Conclusion

In the study described above, we explored the viability of a new method for the synthesis of silicon-containing macrocyclic compounds, which utilizes intramolecular photocycloaddition reactions of substrates containing styrene and stilbene reaction centers tethered by bis(dimethylsilylmethyl)benzene chains. The efficiencies and product distributions were determined for reactions promoted under direct irradiation, SET-sensitized and energy transfer-sensitized conditions. The

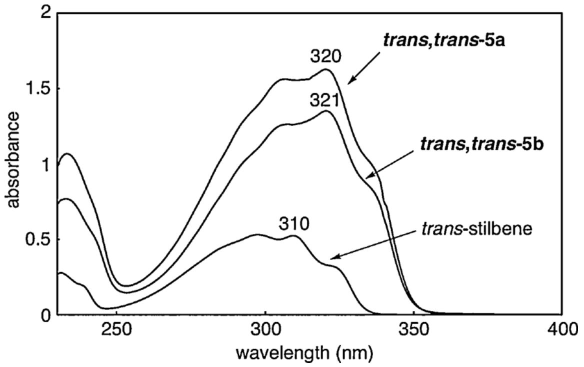


Fig. 5. UV absorption spectra of ***trans,trans*-5a-b** and *trans*-stilbene (2.0×10^{-5} M in CH_2Cl_2).

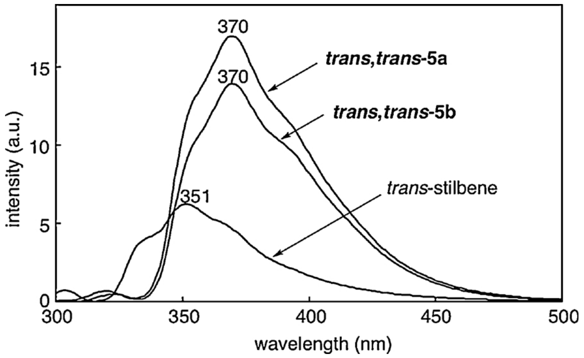


Fig. 6. Fluorescence spectra of ***trans,trans*-5a-b** and *trans*-stilbene (2.0×10^{-5} M in CH_2Cl_2).

results show that intramolecular [2 + 2] photocycloaddition reactions occur in the direct irradiation processes to generate silicon-containing macrocyclic products. The efficiencies of these cycloaddition reactions were found to strongly depend on the distances between two styrene or stilbene double bonds. In addition, the results show that *cis-trans* photoisomerization takes place in photoreactions of the stilbene derivatives, and that *cis-trans* isomerization is the sole pathway followed in triplet-sensitized photoreactions. A competing reaction that produces phenanthrene derivatives occurs when dioxygen is present in stilbene containing solutions being directly irradiated. Overall, the intramolecular photocycloaddition protocol appears to be a valuable strategy for synthesis of silicon-containing macrocyclic compounds.

4. Experimental section

4.1. Materials and equipment

THF was distilled from CaH_2 and then from $Na/Ph_2C{=}O$. CH_3CN was distilled from P_2O_5 and then from CaH_2. Benzene was distilled from CaH_2 and then from Na. Other chemicals were purchased and used after purification by distillation or recrystallization. Compounds **4a-c** were prepared using literature procedures [14,15]. Melting points were determined on a Yanagimoto Micro Melting Point apparatus, Yanaco MP-500. ^1H and ^{13}C NMR spectra were recorded using a Varian MERCURY-300 (300 MHz and 75 MHz, respectively) spectrometer with Me_4Si as an internal standard. IR spectra were determined using a Jasco FT/IR-230 spectrometer. UV–vis spectra were recorded using a Shimadzu UV-160 A spectrophotometer. Fluorescence spectra were recorded using a Jasco FP-6300 spectrophotometer. Mass spectra (EI) were recorded on a SHIMADZU GCMS-QP5050 operating in the electron impact mode (70 eV) equipped with GC-17 A and DB-5MS column (J&W Scientific Inc., Serial: 8696181). HPLC separations were performed on a recycling preparative HPLC equipped with Jasco PU-986 pump, Shodex RI-72 differential refractometer, Megapak GEL 201Cp and 201CP columns (GPC), using $CHCl_3$ as an eluent. Column chromatography was conducted by using Kanto-Chemical Co. Ltd., silica gel 60 N (spherical, neutral, 0.063–0.200 mm).

4.2. Preparation of *trans,trans*-5a

To an argon-purged, stirred CH_3CN (1 mL) solution of 1,2-bis[(4-vinylphenylmethyl)dimethylsilylmethyl]benzene (**4a**, 504 mg, 1.2 mmol [14,15]) and iodobenzene (491 mg, 2.4 mmol) were added Et_3N (1 mL) and $Pd(OAc)_2$ (5 mg, 0.022 mmol). The solution was stirred at reflux for 12 h and filtered to remove Pd catalysts. To the filtrate were added benzene and H_2O. The organic layer was separated, dried over Na_2SO_4 and concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography (benzene:AcOEt = 5:1) followed by recycling preparative HPLC (GPC) and recrystallization from EtOH to produce *trans,trans*-1,2-bis{[4-(2-phenylvinyl)phenylmethyl]dimethylsilylmethyl}benzene (***trans,trans*-5a**, 186 mg, 26% yield). Colorless solid; mp 142–144 °C; ^1H NMR (300 MHz, $CDCl_3$) δ –0.08 (s, 12 H), 1.93 (s, 4 H), 2.09 (s, 4 H), 6.88–6.95 (m, 4 H), 6.96 (d, J = 8.2 Hz, 4 H), 7.00 (d, J = 16.9 Hz, 2 H), 7.07 (d, J = 16.5 Hz, 2 H), 7.23 (t, J = 7.0 Hz, 2 H), 7.34 (t, J = 7.2 Hz, 4 H), 7.36 (d, J = 8.2 Hz, 4 H), 7.47 (d, J = 7.1 Hz, 4 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ –3.36, 22.30, 25.81, 124.06, 126.23, 126.39, 127.04, 127.17, 128.37, 128.52, 128.56, 128.93, 133.15, 136.30, 137.49, 139.68 ppm.

4.3. Preparation of *trans,trans*-5b

To an argon-purged, stirred CH_3CN (10 mL) solution of 1,3-bis[(4-vinylphenylmethyl)dimethylsilylmethyl]benzene (**4b**, 4.96 g, 11.6 mmol [14,15]) and iodobenzene (5.08 g, 24.9 mmol) were added Et_3N (8 mL) and $Pd(OAc)_2$ (50 mg, 0.22 mmol). The solution was stirred at reflux for 12 h and filtered to remove Pd catalysts. To the filtrate were added benzene and H_2O. The organic layer was separated, dried over Na_2SO_4 and concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography (benzene:AcOEt = 5:1) followed by recycling preparative HPLC (GPC) and recrystallization from EtOH to produce *trans,trans*-1,3-bis{[4-(2-phenylvinyl)phenylmethyl]dimethylsilylmethyl}benzene (***trans,trans*-5b**, 2.5 g, 34% yield). Colorless solid; mp 97–100 °C; ^1H NMR (300 MHz, $CDCl_3$) δ –0.05 (s, 12 H), 2.06 (s, 4 H), 2.12 (s, 4 H), 6.62 (s, 1 H), 6.73 (dd, J = 7.5, 1.6 Hz, 2 H), 6.97 (d, J = 8.1 Hz, 4 H), 7.02 (d, J = 16.4 Hz, 2 H), 7.08 (t, J = 7.4 Hz, 1 H), 7.08 (d, J = 16.9 Hz, 2 H), 7.23 (t, J = 10.5 Hz, 2 H), 7.34 (t, J = 6.7 Hz, 4 H), 7.37 (d, J = 8.2 Hz, 4 H), 7.49 (d, J = 7.1 Hz, 4 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ –3.56, 25.23, 25.40, 124.01, 126.21, 126.36, 127.00, 127.16, 127.95, 127.97, 128.37, 128.51, 128.59, 133.11, 137.49, 139.52, 139.68 ppm; IR (KBr) 836, 1074, 1249, 1597, 2956 cm^{-1}.

4.4. Photoreactions

Photoreactions shown in Schemes 2 and 3 and summarized in Table 1 were carried out by using a benzene (8 mL) solution of substrate (**4a-c**, 0.02 M) in a cylindrical Pyrex tube (φ = 8 mm). The solution was degassed by argon bubbling for 10 min and then the vessel was sealed. The solution was irradiated (> 280 nm) by using a 300 W high-pressure mercury lamp (Eikosha, PIH-300) at rt, maintained by using circulated cooling water.

Experiments shown in Schemes 4–6, and summarized in Figs. 3 and 4 were carried out by using a benzene (8 mL) or benzene-d_6 (0.6 mL) solution of substrate (***trans,trans*-5a-b,** 0.02 M) in a cylindrical Pyrex tube (φ = 8 mm) or a NMR tube (Wilmad 528-PP-8, φ = 5 mm). The solution was degassed by argon bubbling for 10 min and then the vessel was sealed. The solution was irradiated by using a 500 W Xenon lamp (M. Watanabe & Co., Ltd., WACOM Hx-500) with UV-29 (> 290 nm) or UV-36 (> 360 nm, Scheme 5) filters.

The crude photolysates were separated and purified by using silica gel column chromatography and/or recycling preparative HPLC.

4.4.1. (2S*,5R*)-11,11,20,20-Tetramethyl-11,20-disilapentacyclo [20.2.2.$2^{6,9}$.$0^{13,18}$.$0^{2,5}$]octacosa-6,8,13(18),14,16,22,24,25,27-nonaene (6a)

Colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ –0.19 (s, 6 H), –0.13 (s, 6 H), 1.85 (s, 4 H), 2.03 (s, 4 H), 2.40–2.44 (m, 4 H), 3.93–3.94 (m, 2 H), 6.74 (d, J = 8.1 Hz, 4 H), 6.81 (d, J = 8.1 Hz, 4 H), 6.87–6.96 (m, 4 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ –3.85, –3.67, 21.37, 23.52, 45.17, 123.75, 127.04, 127.78, 129.60, 135.74, 136.72, 136.89 ppm; MS (EI) m/z (relative intensity, %) 73 (82), 207 (52), 292 (100), 454 (M^+, 20).

4.4.2. (2S,5R*)-11,11,19,19-Tetramethyl-11,19-disilapentacyclo[19.2.2.$2^{6,9}$.$1^{13,17}$.$0^{2,5}$]octacosa-6,8,13(28),14,16,21,23,24,26-nonaene* ***(6b)***

Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (s, 6 H), 0.08 (s, 6 H), 1.87 (m, 8 H), 2.40–2.42 (m, 4 H), 3.94 (m, 2 H), 6.20 (s, 1 H), 6.69 (dd, J = 7.5, 1.6 Hz, 2 H), 6.82 (m, 8 H), 7.04 (t, J = 7.5 Hz, 1 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ –2.24, –2.09, 23.56, 23.74, 24.17, 45.36, 123.45, 127.52, 128.00, 128.07, 129.39, 136.90, 137.05, 139.33 ppm. MS (EI) *m/z* (relative intensity, %) 73 (100), 221 (44), 291 (45), 454 (M^+, 45).

4.4.3. 11,11,19,19,34,34,42,42-Octamethyl-11,19,34,42-tetrasilanonacyclo[42.2.2.$2^{29,32}$.$2^{21,24}$.$2^{6,9}$.$1^{36,40}$.$1^{13,17}$.$0^{25,28}$.$0^{2,5}$]pentacontahexa-6,8,13,15,17(51),21,23,29,31,36(56),37,39,44,46,47,49,52,54-octadecaene (7)

This product could not be isolated, however, was assigned and quantified by δ 2.82–2.93 ppm (multiplet, benzylic hydrogen on *trans*-cyclobutane) and δ 3.96–4.02 ppm (multiplet, benzylic hydrogen on *cis*-cyclobutane) in ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of a mixture with **6b**.

4.4.4. 1,2-Bis[4-({4-[(4-vinylphenylmethyl)dimethylsilylmethyl]phenylmethyl}dimethylsilylmethyl)phenyl]cyclobutane (8)

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.10-0.30 (m, 24H, *cis* + *trans*), 1.51–2.51 (m, 16H, *cis* + *trans*), 3.14 (dt-like, J = 15.6, 6.7 Hz, 2H, *trans*), 3.76 (quint-like, J = 7.6 Hz, 2H, *cis*), 5.19 (d-like, J = 11.0 Hz, 2H, *cis* + *trans*), 5.71 (d-like, J = 17.6 Hz, 2H, *cis* + *trans*), 6.15–7.31 (m, 26H, *cis* + *trans*) ppm.

4.4.5. (2S,3R*,4S*,5R*)-11,11,19,19-Tetramethyl-3,4-diphenyl-11,19-disilapentacyclo[19.2.2.$2^{6,9}$.$1^{13,17}$.$0^{2,5}$]octacosa-6,8,13(28),14,16,21,23,24,26-nonaene* ***(cis,trans,cis-9b)***

^{1}H NMR (300 MHz, C_6D_6) δ –0.05 (s, 6 H), –0.01(s, 6 H), 1.84 (s, 8 H), 4.33 (d, J = 6.5 Hz, 2 H), 4.39 (d, J = 6.5 Hz, 2 H), 6.08 (s, 1 H), 6.62 (d, J = 7.7 Hz, 2 H), 6.81(d, J = 8.1 Hz, 4 H), 6.94 (d, J = 8.1 Hz, 4 H), 6.98–7.17 (m, 11 H) ppm.

Acknowledgements

This investigation was supported financially by the Corporation of Innovative Technology and Advanced Research in Evolutional Area (CITY AREA) from the Wakayama Technology Promotion Foundation. This investigation was also supported financially by a Grant-in-Aid for Scientific Research (KAKENHI) on Priority Areas 'Multi-Element Cyclic Compounds' (13029101 and 14044092), '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.

References

[1] J. Nishimura, H. Doi, E. Ueda, A. Ohbayashi, A. Oku, J. Am. Chem. Soc. 109 (1987) 5293–5295.
[2] J. Nishimura, A. Ohbayashi, H. Doi, K. Nishimura, A. Oku, Chem. Ber. 121 (1988) 2019–2024.
[3] J. Nishimura, A. Ohbayashi, Y. Wada, A. Oku, S. Ito, A. Tsuchida, M. Yamamoto, Y. Nishijima, Tetrahedron Lett. 29 (1988) 5375–5378.
[4] J. Nishimura, M. Takeuchi, H. Takahashi, E. Ueda, Y. Matsuda, A. Oku, Bull. Chem. Soc. Jpn. 62 (1989) 3161–3166.
[5] J. Nishimura, Y. Horikoshi, Y. Wada, H. Takahashi, S. Machino, A. Oku, Tetrahedron Lett. 30 (1989) 5439–5442.
[6] S. Inokuma, T. Yamamoto, J. Nishimura, Tetrahedron Lett. 31 (1990) 97–100.
[7] S.A. Fleming, S.C. Ward, Tetrahedron Lett. 33 (1992) 1013–1016.
[8] J. Nishimura, M. Takeuchi, M. Koike, H. Sakamura, O. Yamashita, J. Okada, N. Takaishi, Bull. Chem. Soc. Jpn. 66 (1993) 598–606.
[9] Y. Nakamura, M. Matsumoto, Y. Hayashida, J. Nishimura, Tetrahedron Lett. 38 (1997) 1983–1986.
[10] J. Nishimura, Y. Nakamura, Y. Hayashida, T. Kudo, Acc. Chem. Res. 33 (2000) 679–686.
[11] K. Nakanishi, K. Mizuno, Y. Otsuji, J. Chem. Soc. Perkin Trans. 1 (1990) 3362–3363.
[12] K. Mizuno, K. Nakanishi, Y. Otsuji, T. Hayamizu, H. Maeda, T. Adachi, A. Ishida, S. Takamuku, J. Photosci. 10 (2003) 121–126.
[13] H. Maeda, H. Yagi, K. Mizuno, Chem. Lett. 33 (2004) 388–389.
[14] H. Maeda, K. Nishimura, K. Mizuno, M. Yamaji, J. Oshima, S. Tobita, J. Org. Chem. 70 (2005) 9693–9701.
[15] H. Maeda, R. Hiranabe, K. Mizuno, Tetrahedron Lett. 47 (2006) 7865–7869.
[16] R. Corriu, J. Masse, Bull. Soc. Chim. Fr. (1974) 3045–3048.
[17] J.T. Anhaus, V.C. Gibson, W. Clegg, S.P. Collingwood, Organometallics 12 (1993) 1780–1789.
[18] B. König, M. Rödel, P. Bubenitschek, P.G. Jones, Angew. Chem. Int. Ed. Engl. 34 (1995) 661–662.
[19] F.-Q. Liu, G. Harder, T.D. Tilley, J. Am. Chem. Soc. 120 (1998) 3271–3272.
[20] M. Yoshida, M. Goto, F. Nakanishi, Organometallics 18 (1999) 1465–1470.
[21] E. Kwon, K. Sakamoto, C. Kabuto, M. Kira, Chem. Lett. 29 (2000) 1416–1417.
[22] N. Mézailles, N. Maigrot, S. Hamon, L. Ricard, F. Mathey, P.L. Floch, J. Org. Chem. 66 (2001) 1054–1056.
[23] M. Unno, K. Negishi, H. Matsumoto, Chem. Lett. 30 (2001) 340–341.
[24] S. Kyushin, T. Kitahara, R. Tanaka, M. Takeda, T. Matsumoto, H. Matsumoto, Chem. Commun. (2001) 2714–2715.
[25] H. Zhang, K.T. Lam, Y.L. Chen, T. Mo, C.C. Kwok, W.Y. Wong, M.S. Wong, A.W.M. Lee, Tetrahedron Lett. 43 (2002) 2079–2082.
[26] K. Negishi, M. Unno, H. Matsumoto, Chem. Lett. 33 (2004) 430–431.
[27] J.C. Roberts, J.A. Pincock, J. Org. Chem. 71 (2006) 1480–1492.
[28] K. Nakanishi, K. Mizuno, Y. Otsuji, J. Chem. Soc. Chem. Commun. (1991) 90–92.
[29] C. Pac, A. Nakasone, H. Sakurai, J. Am. Chem. Soc. 99 (1977) 5806–5808.
[30] T. Majima, C. Pac, A. Nakasone, H. Sakurai, J. Am. Chem. Soc. 103 (1981) 4499–4508.
[31] Y. Yoshimi, J. Photochem. Photobiol. A: Chem. 342 (2017) 116–130.
[32] H. Görner, K.-D. Warzecha, M. Demuth, J. Phys. Chem. A 101 (1997) 9964–9973.
[33] F. Bayrakçeken, Spectrochim. Acta Part A 71 (2008) 603–608.
[34] E.J.J. Groenen, W.N. Koelman, J. Chem. Soc. Faraday Trans. 2 (75) (1979) 58–68.
[35] W.-Q. Zhou, H.-P. Peng, J.-K. Xu, H.-Y. Xia, S.-Z. Pu, Polym. Int. 57 (2008) 92–98.
[36] H. Shechter, W.J. Link, G.V.D. Tiers, J. Am. Chem. Soc. 85 (1963) 1601–1605.
[37] D.H. Waldeck, Chem. Rev. 91 (1991) 415–436.
[38] T. Arai, K. Tokumaru, Chem. Rev. 93 (1993) 23–39.
[39] J. Weijun, L. Changsong, Anal. Chem. 65 (1993) 863–865.
[40] J. Saltiel, G.-E. Khalil, K. Schanze, Chem. Phys. Lett. 70 (1980) 233–235.
[41] H. Görner, J. Phys. Chem. 93 (1989) 1826–1832.
[42] F.B. Mallory, C.W. Mallory, Org. React. 30 (1984) 1–456.