

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 PdCl₂/CCl₄ 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 CH₂Cl₂ 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 ¹H 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.

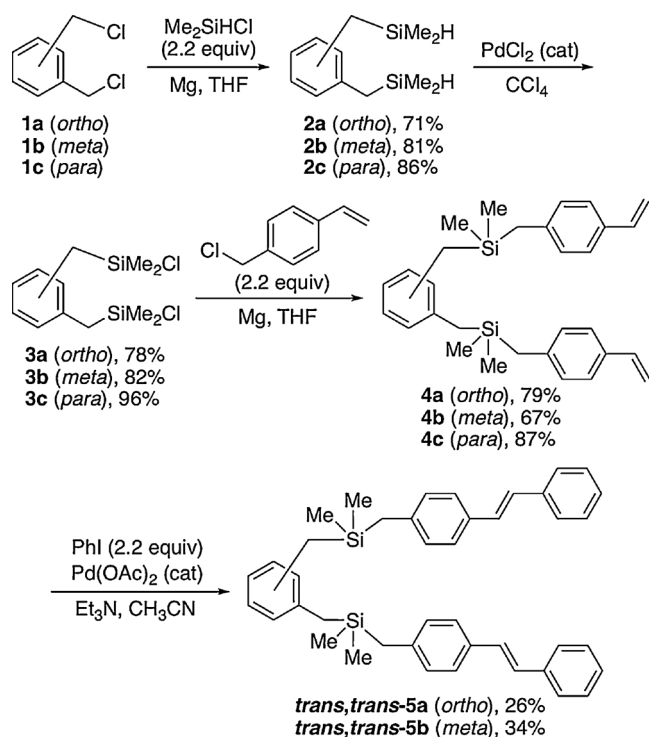
E-mail addresses: maeda-h@se.kanazawa-u.ac.jp (H. Maeda), kmizuno@ms.naist.jp (K. Mizuno).

<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

Available online 23 June 2018

1010-6030/ © 2018 Elsevier B.V. All rights reserved.



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

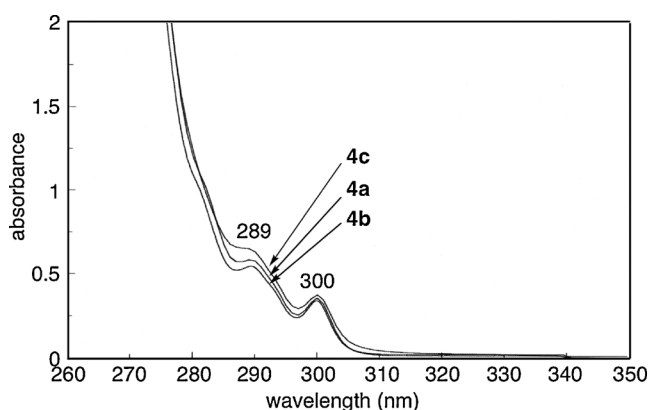
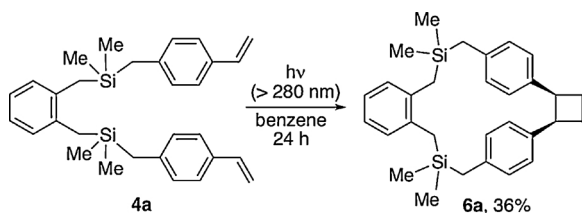


Fig. 1. UV absorption spectra of **4a-c** (1.0×10^{-4} M in CH_2Cl_2).



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 ^1H 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.

The use of photosensitizers to promote reaction of **4a** was explored

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	<i>p</i> -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.

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. ^1H 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*-**9a-b** and *cis,cis*-**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 ^1H 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 (2H) and 4.39 ppm (2H) 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 ^1H 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 ^1H 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]

Download English Version:

<https://daneshyari.com/en/article/6492417>

Download Persian Version:

<https://daneshyari.com/article/6492417>

[Daneshyari.com](https://daneshyari.com)