

# Synthesis of a novel silicon-bridged [2.2]metacyclophan-9-ene and its photolytic transannular reaction

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Received 10 August 2005; received in revised form 10 November 2005; accepted 22 November 2005

Available online 27 December 2005

## Abstract

A novel [2.2]metacyclophane in which two benzene rings are linked together with a carbon–carbon double bond and a disilane unit was prepared. Photolysis of the cyclophane in the presence of oxygen afforded the 4,5-dihydro-4,5-disilapyrene derivative via a transannular dehydrogenation reaction.

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**Keywords:** [2.2]Metacyclophan-9-ene; Transannular reaction; Photolysis

## 1. Introduction

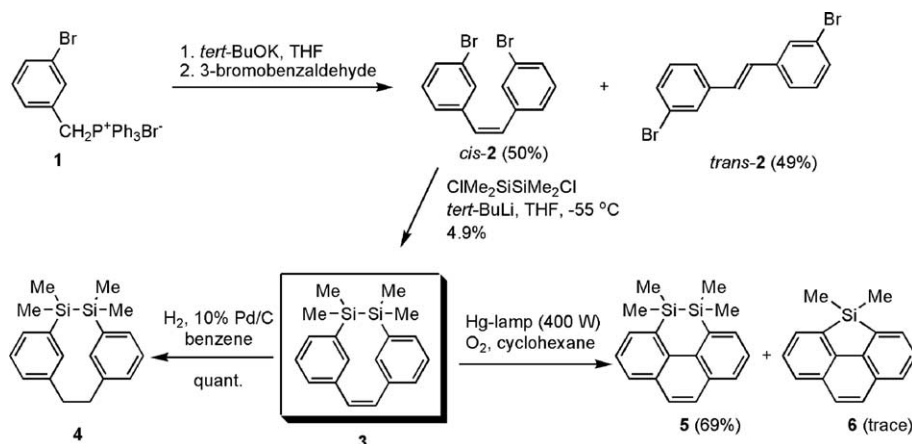
Over the years, much attention has been drawn to the chemistry of [2.2]metacyclophanes due to their intriguing physical and chemical properties such as an unusual feature of the  $^1\text{H}$  NMR spectra, the transannular interactions and reactions, and the considerable strain exerted in the rigid 10-membered ring, mainly based on their unique architecture [1]. On the other hand, there have been only a few reports concerning the [2.2]metacyclophanes involving silicon atoms in their bridge. The first synthesis of tetrasil[2.2]metacyclophane was achieved by Sakurai and co-workers [2]. Later, we reported the synthesis of [2.2]metacyclophanes containing two or three silicon atoms located at various positions of the bridges [3]. In this paper we would like to describe the synthesis, some structural aspects, and photolytic transannular reaction of a novel [2.2]metacyclophane in which two benzene rings are bridged by a carbon–carbon double bond and a disilane unit. The observed transannular ring closure is the first to take place in the silicon-bridged [2.2]metacyclophane system.

## 2. Results and discussion

As shown in Scheme 1, the synthesis of 1,1,2,2-tetramethyl-1,2-disila[2.2]metacyclophan-9-ene (**3**) began with Wittig olefination between 3-bromobenzylidene triphenylphosphorane, prepared in situ from phosphonium salt **1** and potassium *tert*-butoxide, and 3-bromobenzaldehyde. The desired 3,3'-dibromo-*cis*-stilbene (*cis*-**2**) was obtained in 50% yield along with 49% yield of the corresponding *trans* isomer. Ring closure of the dibromostilbene *cis*-**2** with 1,2-dichlorodisilane in the presence of *tert*-butyllithium was carried out at  $-55\text{ }^\circ\text{C}$  under high-dilution conditions to give novel silicon-bridged [2.2]metacyclophan-9-ene (**3**) in 4.9% yield based on the consumed dibromide. The structure of compound **3** was determined by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR and high-resolution mass spectra. Further confirmation of the structure was carried out by catalytic hydrogenation of the C–C double bond of **3** in the presence of 10% palladium on carbon to give quantitative yield of 1,1,2,2-tetramethyl-1,2-disila[2.2]metacyclophane (**4**) which we previously prepared in a different way [3].

It is well-known that the [2.2]metacyclophanes adopt a step-like conformation where two benzene rings are arranged in parallel planes. As a result, the NMR signals of the intra-annular aryl protons, the 8,16-protons, resonate

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Scheme 1. Synthesis and reactions of 1,2-disila[2.2]metacyclophan-9-ene (3).

at unusually high-field due to the diamagnetic ring-current effect of the opposite benzene ring. The  $^1\text{H}$  NMR spectra of the silicon-bridged [2.2]metacyclophane (4) showed the inner aryl proton resonances at 5.33 ppm as one broad triplet. Furthermore, the signals for the two methyl groups attached to the silicon atom and the methylene protons of the ethylene bridge appeared as two singlets and an AA'BB' system, respectively, indicating the stepped conformation of the cyclophane 4 is rigid at room temperature. On the other hand, the signals for the inner aryl protons of the [2.2]metacyclophan-9-ene (3) appeared at 6.83 ppm in the normal aromatic region and the two methyl groups attached to the silicon atom resonated at 0.18 ppm as one broad singlet. We assumed that the introduction of the bridging double bond made a slight change in the step-like structure of the [2.2]metacyclophane system so that the ring inversion would become feasible even at room temperature. Using variable temperature NMR spectroscopy, the energy barrier to ring inversion for the cyclophane 3 could be estimated to be 45 kJ/mol from the maximum frequency separation (217 Hz) of the methyl proton resonances and their coalescence point (235 K) [4]. The value is considerably less than that for cyclophane 4 (66 kJ/mol).

The silicon-bridged [2.2]metacyclophan-9-ene (3) has an absorption spectrum similar to that of *cis*-stilbene. An absorption band around 311 nm ( $\epsilon_{\text{max}} = 3616$ ) in hexane attributed to  $\pi\text{-}\pi^*$  transition is 28 nm longer in wavelength than that of *cis*-stilbene, suggesting that a more co-planar arrangement of the two benzene rings is feasible by introducing an additional linkage, the disilane bridge, into the distorted *cis*-stilbene system.

One other striking feature of [2.2]metacyclophane chemistry is transannular reactions. When a solution of 1,2-disila[2.2]metacyclophan-9-ene (3) in cyclohexane ( $6.8 \times 10^{-3}$  M) in a quartz tube was irradiated with a 400 W medium-pressure mercury lamp under an oxygen atmosphere at room temperature for 1 h, an intramolecular transannular dehydrogenation reaction between the 8 and 16-positions took place to give 69% yield of 4,5-dihydro-4,5-disilapyrene derivative 5 based on the consumed start-

ing material along with a trace amount of 4-hydro-4-silacyclopenta[def]phenanthrene derivative 6. Other silicon-bridged [2.2]metacyclophanes containing various numbers of silicon atoms at various positions, prepared previously by us [3], were also subjected to the above photoreaction conditions; however, all attempts resulted in no reaction or gave a complex mixture. It can be, therefore, presumed that the introduction of the bridging double bond facilitates the co-planar arrangement of the two benzene nuclei favorable to transannular ring closure because of the planarity of the valences at  $\text{sp}^2$ -hybridized carbons.

The obtained fused tetracycles 5 and 6 containing silicon atoms are new compounds and their structures are determined by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  (only for 5) NMR and high-resolution mass spectra. The formation of compound 6 can be explained by a photo-induced extrusion of dimethylsilylene from 4,5-dihydro-4,5-disilapyrene (5). Similar ring reduction accompanied by the generation of divalent species has been reported by Kira and co-workers, where the photolysis of 9,10-dihydro-9,10-disilaphenanthrene and its germanium analogue afforded the corresponding fluorene derivatives [5].

In summary, we have demonstrated the synthesis and some structural aspects of novel 1,2-disila[2.2]metacyclophan-9-ene (3). It was found that the introduction of a bridging double bond provided some flexibility in the 10-membered ring to facilitate the ring inversion. Upon photolysis the unprecedented transannular ring closure of silicon-bridged [2.2]metacyclophane took place to afford a 4,5-dihydro-4,5-disilapyrene derivative.

### 3. Experimental

#### 3.1. General

Melting points are uncorrected.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectra were measured at 400.0, 100.6, and 79.5 MHz, respectively. All chemical shifts are reported as  $\delta$  values (ppm) relative to residual chloroform ( $\delta_{\text{H}}$  7.26), the central peak of deuteriochloroform ( $\delta_{\text{C}}$  77.0), or tetramethylsilane

( $\delta_{\text{Si}}$  0.00). High-resolution mass spectra (HRMS) were determined using perfluorokerosene as an internal standard. Absorption spectra were measured using a Shimadzu UV-1700 UV–visible spectrophotometer. Solvents and reagents were of commercial grade and were purified if necessary.

### 3.2. 3,3'-Dibromo-*cis*-stilbene (*cis*-2)

To a suspension of phosphonium salt **1** (47.7 g, 93.1 mmol) in THF (100 mL) were added successively potassium *tert*-butoxide (12.6 g, 112 mmol) and, after 30 min, a solution of 3-bromobenzaldehyde (17.2 g, 93.0 mmol) in THF (100 mL). After being stirred overnight, the precipitated solids were removed by filtration using a Celite pad. The filtrate was then concentrated in vacuo and trituration of the residue with hexane furnished pure 3,3'-dibromo-*trans*-stilbene (15.3 g) in 49% yield. The hexane solution containing the desired *cis*-isomer was submitted to flash column chromatography on silica gel (hexane) to give the title compound *cis*-**2** (15.6 g) in 50% yield as a colorless oil [6].  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.55 (s, 2H), 7.05–7.14 (m, 4H), 7.31–7.38 (m, 4H).

### 3.3. 1,1,2,2-Tetramethyl-1,2-disila[2.2]metacyclophan-9-ene (**3**)

To a solution of 1.50 M *tert*-butyllithium in pentane (48.0 mL, 72.0 mmol) and THF (100 mL) was added dropwise a solution of *cis*-**2** (10.1 g, 30.0 mmol) and 1,1,2,2-tetramethyl-1,2-dichlorosilane (6.97 g, 37.2 mmol) in THF (200 mL) over a period of 200 min under an argon atmosphere at  $-55^\circ\text{C}$ . After being stirred at room temperature overnight, the reaction mixture was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$  and the organic layer was dried over  $\text{MgSO}_4$ . After removal of the solvent, the residue was purified by repeated column chromatography on silica gel (hexane) and RP-18 (MeOH/ $\text{H}_2\text{O}$  = 95/5) to afford 4.9% yield of the title compound **3** (275 mg) as colorless crystals, m.p.  $90$ – $91^\circ\text{C}$ , based on recovered *cis*-**2** (3.76 g, 11.1 mmol).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.18 (br s, 12H), 6.62 (s, 2H), 6.83 (s, 2H), 7.11–7.14 (m, 2H), 7.25–7.33 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$   $-6.4$ , 128.0, 128.2, 130.7, 131.8, 135.0, 135.3, 136.7.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ )  $\delta$   $-17.0$ . HRMS (EI, 70 eV)  $m/z$  294.1272 ( $\text{M}^+$ , calcd. for  $\text{C}_{18}\text{H}_{22}\text{Si}_2$  294.1260). UV (hexane)  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon_{\text{max}}$ ) 311 (3616), 248 (sh, 26777). Anal. Calc. for  $\text{C}_{18}\text{H}_{22}\text{Si}_2$ : C, 73.40; H, 7.53. Found: C, 73.07; H, 7.49%.

### 3.4. 1,1,2,2-Tetramethyl-1,2-disila[2.2]metacyclophane (**4**)

A solution of 1,2-disila[2.2]metacyclophan-9-ene (**3**) (10.1 mg, 0.0343 mmol) in benzene (2 mL) was hydrogenated in the presence of 10% palladium on carbon (10.1 mg) for 1 h. After removal of the catalyst, the solvent was concentrated to afford quantitative yield of the title

compound **4** as an oil, which solidified upon standing. Recrystallization from hexane gave colorless plates, m.p.  $50$ – $51.5^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.02 (br s, 6H), 0.45 (br s, 6H), 2.24 (br d,  $J = 8$  Hz, 2H), 3.09 (br d,  $J = 8$  Hz, 2H), 5.33 (s, 2H), 7.18–7.22 (m, 2H), 7.28–7.37 (m, 4H).  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ )  $\delta$   $-17.9$ .  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$   $-6.5$ ,  $-6.2$ , 39.2, 128.0, 128.2, 130.7, 134.7, 138.5, 139.0. HRMS (EI, 70 eV)  $m/z$  296.1429 ( $\text{M}^+$ , calcd. for  $\text{C}_{18}\text{H}_{24}\text{Si}_2$  296.1419). Anal. Calc. for  $\text{C}_{18}\text{H}_{24}\text{Si}_2$ : C, 72.90; H, 8.16. Found: C, 72.60; H, 8.12%.

### 3.5. Photolytic transannular reaction of 1,2-disila[2.2]metacyclophan-9-ene (**3**)

A solution of 1,2-disila[2.2]metacyclophan-9-ene (**3**) (10.0 mg, 0.0340 mmol) in cyclohexane (5 mL) in a quartz tube was irradiated with a 400 W medium-pressure mercury lamp under an oxygen atmosphere at room temperature for 1 h. After removal of the solvent, the residue was chromatographed on silica gel to give 69% yield of 4,4,5,5-tetramethyl-4,5-dihydro-4,5-disilapyrene (**5**, 5.50 mg) as a colorless oil based on recovered cyclophane **3** (2.00 mg, 0.00680 mmol, 20%) along with a trace amount of 4,4-dimethyl-4-hydro-4-silacyclopenta[*def*]phenanthrene (**6**) as a colorless oil. **5**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.37 (s, 12H), 7.51–7.55 (m, 2H), 7.69 (s, 2H), 7.81–7.87 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$   $-3.9$ , 125.4, 128.1, 130.7, 133.0, 133.4, 136.6, 136.9.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ )  $\delta$   $-26.5$ . HRMS (EI, 70 eV)  $m/z$  292.1094 ( $\text{M}^+$ , calcd. for  $\text{C}_{18}\text{H}_{20}\text{Si}_2$  292.1104).

An analytical sample of compound **6** was isolated from a combined reaction mixture obtained by several runs.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.55 (s, 6H), 7.58–7.63 (m, 2H), 7.76 (s, 2H), 7.84–7.90 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$   $-2.9$ , 126.0, 126.9, 127.7, 129.4, 130.2, 137.8, 141.8. HRMS (EI, 70 eV)  $m/z$  235.0928 [ $(\text{M} + \text{H})^+$ , calcd. for  $\text{C}_{16}\text{H}_{15}\text{Si}$  235.0943].

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