1-Aryl-Substituted Cage Molecules ArC($(SiMe_2SiMe_2)_3$)CR: Preparation, Properties, and Application to Liquid Crystalline Compounds

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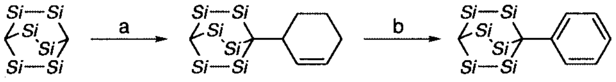
Phenyl groups were successively introduced at the bridgehead positions of cage compound $HC(SiMe_2SiMe_2)_3CH$ via deprotonation–cyclohexenylation–dehydrogenation. UV absorption spectra of the cage compounds suggested the possibility of electronic interaction between the cage and aromatic moieties. Bromination of the phenylated cage molecule gave a *p*-bromo derivative that was transformed to liquid crystalline compounds.

We recently reported that UV spectra of 1,2,4,5-tetrasilacyclohexane and 2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane **1** demonstrated a bathochromic shift of absorption maxima originated from Si–Si σ-bonds when dimensions of the molecular structure increased, and this observation suggests the possibility of three-dimensional σ-conjugation.[1,2] Furthermore, functionalization at a bridgehead position of **1** was achieved by deprotonation with a superbase consisting of BuLi and *t*-BuOK followed by trapping with an electrophile, and such derivatives with a silyl or a stannyl group at the bridgehead also exhibited a red shift of UV absorption maxima compared to parent compound **1**.

In view of electronic interaction between the cage moiety and a substituent at the bridgehead, 1-aryl-substituted derivatives are intriguing since electronic interaction between cage σ-electrons and aromatic π-electrons is expected.[3] Besides, such polysilacage compounds may become to be novel liquid crystalline compounds (LCs), because a bicyclo[2.2.2]octane system possessing an aryl group is known to function as a mesogen of LCs.[4] However, an indirect strategy was necessary to prepare those molecules, because direct coupling of an aryl group to **1** was difficult to perform.[5] We report here three-step preparation and properties of 1-aryl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]-octanes as well as transformation of the arylated cage molecule to liquid crystalline compounds.



1 (*Si* = $SiMe_2$) **2** **3**

a) BuLi/*t*-BuOK (4 molar equiv), THF, –42 °C,
then, 3-bromocyclohexene, 79%.
b) oxidant, solvent.

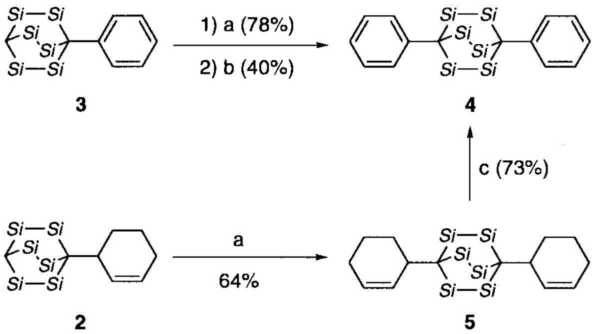
Scheme 1. Synthesis of 1-phenyl cage compound **3**.

Treatment of **1** with an excess amount of a superbase in THF at –42 °C followed by the addition of 3-bromocyclohexene produced cyclohexenyl-substituted cage compound **2** in 79% yield (Scheme 1, step a). Subsequently, dehydrogenative aromatization of the cyclohexenyl group was examined (step b). The results are shown in Table 1. First, oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in benzene at 80 °C gave 1-phenyl cage compound **3** in 38% yield with recovery of **2** (28%) (Entry 1). The yield of **3** increased to 59% when the same oxidation was done in refluxing toluene, while the oxidation in xylene at 140 °C afforded **3** in 49% yield (Entries 2 and 3). Use of *o*-chloranil as an oxidant in benzene turned out to be the most effective for the preparation of **3** (Entry 4).

Table 1. Oxidation of **2** (step b)

Entry	Oxidant (molar equiv)	Solvent	Temp. /°C	Yield of **3**/%	Recovery of **2**/%
1	DDQ (2.3)	benzene	80	38	28
2	DDQ (2.4)	toluene	110	59	24
3	DDQ (40)	xylene	140	49	0
4	*o*-chloranil (2.3)	benzene	80	66	31
5	*o*-chloranil (2.4)	toluene	110	57	37

The phenylation procedure when applied to **3** yielded 1,4-diphenylated cage compound **4** in 31% yield (2 steps) as illustrated in Scheme 2. Alternatively, **4** was synthesized in 47% yield (2 steps) by dehydrogenation of 1,4-dicyclohexenyl substituted compound **5** prepared from **2** using a superbase and 3-bromocyclohexene.[6] The double aromatization method was better in total efficiency.



a) BuLi/*t*-BuOK (4 molar equiv), THF, – 42 °C,
then 3-bromocyclohexene.
b) DDQ (2.3 molar equiv), benzene, reflux.
c) DDQ (4.4 molar equiv), benzene, reflux.

Scheme 2. Preparation of 1,4-diphenyl cage molecule **4**.

UV absorption spectra of **1**, **3**, **4**, and reference compound $(Me_3Si)_3CPh$[7] were measured in cyclohexane and shown in Figure 1. Since the absorption maxima originated from Si–Si bonds in **3** and **4** were probably overlapped with aromatic E_1 absorption bands, it was impossible to estimate the absorption shift of **3** and **4**.[8] However, aromatic E_2 absorption maxima of **3** (241 nm, ε = 17900) and **4** (241 nm, ε = 30900) exhibited a bathochromic shift in comparison with $(Me_3Si)_3CPh$ (230 nm, ε

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= 13500). Accordingly, it might be reasonable to presume σ–π electronic interaction between the cage moiety and a phenyl ring.

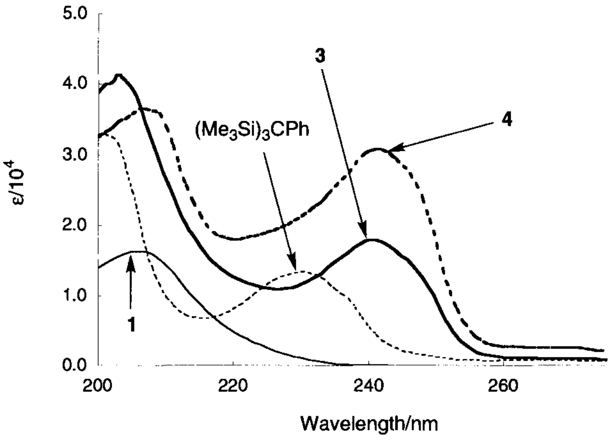
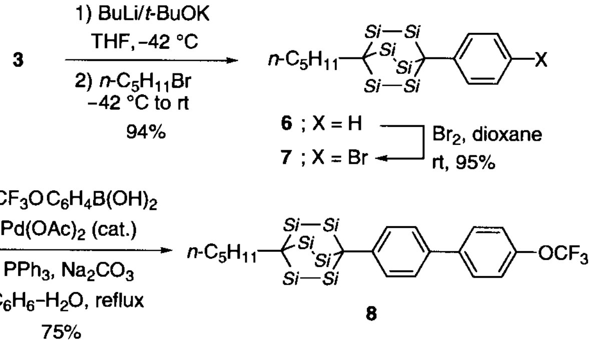


Figure 1. UV absorption spectra of **1**, **3**, **4**, and $(Me_3Si)_3CPh$.

With **3** in hand, we next studied its derivatization to liquid crystalline compounds (Scheme 3). First, **3** was alkylated with pentyl bromide to give **6** in 94% yield. *p*-Bromination of **6** was found to proceed with a bromine–dioxane complex and produce **7** in 95% yield. No oxidation of Si–Si bonds was observed. Palladium-catalyzed cross-coupling reaction of **7** with 4-trifluoromethoxyphenylboronic acid afforded biphenyl-containing cage **8** in 75% yield.



Scheme 3. Conversion of **3** into **6** and **8**.

Differential scanning calorimetry (DSC) charts of **6** and **8** are shown in Figure 2. Upon heating, **6** showed endothermic peaks at 197.1 °C and 237.3 °C. In addition, optical polarization microscopy of **6** at 200 °C exhibited tree texture which is characteristic to discotic hexagonal phase. Similar optical observation of **8** on heating showed double reflection, suggesting anisotropic character.

In summary, we have synthesized 1-aryl- and 1,4-diaryl-substituted cage compounds and shown their UV spectra and application to liquid crystalline compounds. Further studies on arylated cage compounds are in progress.

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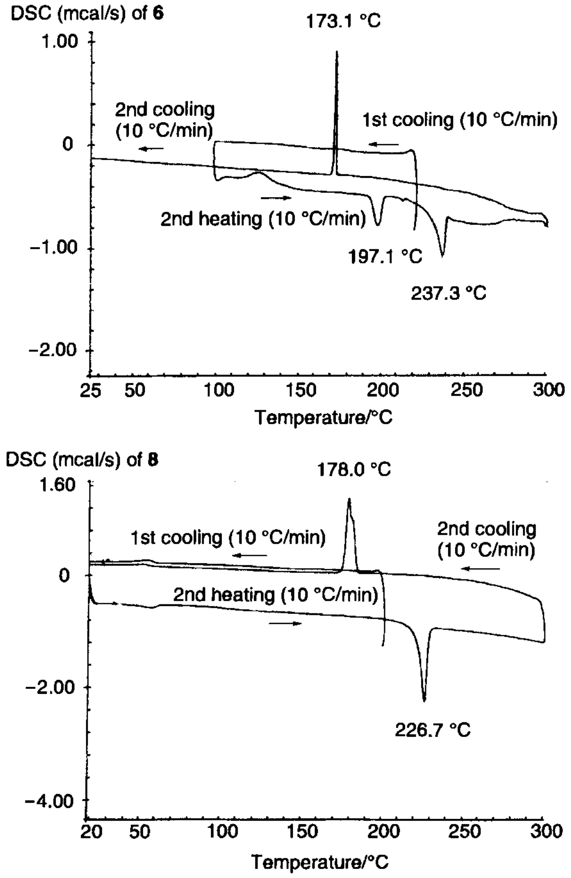

Figure 2. DSC charts of **6** and **8**.

Dedicated to Professor Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

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