A SYNTHESIS OF 5-SILACYCLOTRIVERATRYLENES[†]

Hiroshi Hara, Hiroya Satoh, and Osamu Hoshino*

Faculty of Pharmaceutical Sciences, Science University of Tokyo, Shinjuku-ku,
Tokyo 162, Japan

Abstract---- The dilithio compound (**4**), derived from 4,5-bis(6-bromoveratryl)-veratrol (**3**), reacted with dichlorodimethylsilane to give 5,5-dimethyl-5-silacyclotriveratrylene (**2a**). Similarly, several 5-silacyclotriveratrylenes (**2b**, **2c**, and **2d**) and a methylenedioxy analogue (**6**) were prepared. On the basis of ^{1}H-nmr spectra flexible conformation of the sila-heterocyclic system was elucidated.

Cyclotriveratrylene (**1**) and its analogues have been widely studied because of their interesting properties such as conformational behavior and host compounds.[1] Although many investigations on their synthesis have been reported so far, a few cyclotribenzylene and cyclotriveratrylene derivatives, methylene groups in which were replaced with hetero atom such as oxygen,[2] sulfur,[2,3] or silicon, have been synthesized. Among them, only one example on synthesis of trisilacyclotribenzylene[4] as a silicon containing compound has been reported. Therefore, we have been interested in synthesis of silacyclotriveratrylenes and their conformational behavior. Here we wish to report a first synthesis of 5-silacyclotriveratrylenes (**2**).

Previously, we have reported that bromination of cyclotriveratrylene (**1**) cleaves the ring to give rise to 4,5-bis(6-bromoveratryl)veratrole (**3**).[5] The dibromide (**3**) is anticipated to be a key compound for synthesis of 5-silacyclotriveratrylene; dilithiated compound (**4**) generated from **3** could react with compounds containing silicon-halogen or silicon-oxygen bonds to give silacyclotriveratrylene system.[6]

In order to confirm generation of **4** from **3**, lithiation of **3** was carried out. After addition of *n*-BuLi (2.5 eq.) to tetrahydrofuran solution of **3**[7] at -50°C the mixture was stirred at the same temperature, and then quenched

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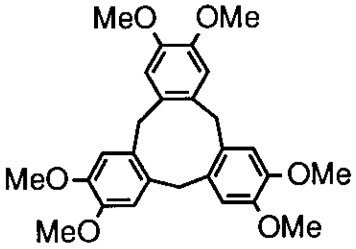
[†] Dedicated to Professor Emeritus Masatomo Hamana on the occasion of his 75th birthday.



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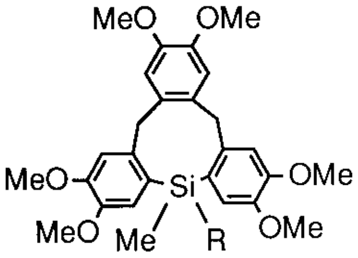
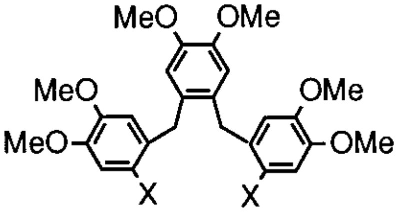


2a: R=-Me

2b: R=$-CH_2Cl$

2c: R=$-CH=CH_2$

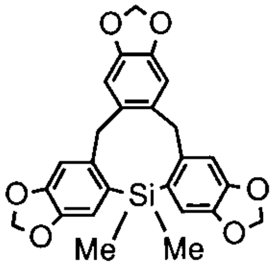
2d: R=



3: X=Br

4: X=Li

5: X=D



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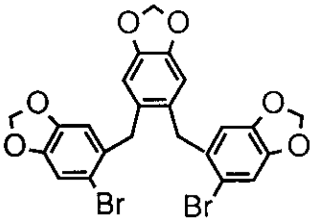

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by excess deuteromethanol to afford a dideutero product (**5**). ^{1}H-Nmr spectrum of **5** showed three singlets of aromatic protons demonstrating formation of the dilithiated compound (**4**).

Thus, reaction of **4** with dichlorodimethylsilane (1.1 eq.) at -50°C for 1 h and subsequent quenching with aqueous ammonium chloride afforded 5,5-dimethylsilacyclotriveratrylene (**2a**),[8] mp 174°C, in 54% yield, ^{1}H-nmr spectrum of which showed six kinds of singlets [δ 0.54 (6H, $SiMe_2$), 3.73 (6H, OMe), 3.87 (12H, OMe), 6.58, 6.72, 6.98 (each 2H, ArH)]. The data verified the symmetrical structure of the sila compound (**2a**). Methylene protons in the ^{1}H-nmr spectrum could not be observed clearly because of being overlapped by numerous protons of six methoxyl groups, while those[9] of cyclotriveratrylene (**1**) appear characteristically as AB pattern to clarify the rigid conformation. This findings suggested that **2a** might exist as a flexible conformation.[1]

For the purpose of revealing the flexible conformation, we tried to synthesize a methylenedioxy analogue (**6**) having no obstructive protons in the region (δ 3.5-4.0) of resonance due to methoxyl protons in the ^{1}H-nmr spectrum. By similar protocol as above, the dibromide (**7**)[8,10] (mp 204°C) was prepared from methylenedioxybebzene and 6-bromopiperonyl alcohol. Analogous treatment of the dibromide (**7**) as described above gave 5,5-dimethyl-5-silacyclotripiperonylene (**6**)[8,10] in 36% yield. As we would expect, in the ^{1}H-nmr spectrum, methylene protons appeared clearly but as broad singlet at δ 3.80 without splitting pattern. Thus, conformation of these sila derivatives must be flexible undoubtedly.

Similarly, reaction of the dilithiated compound (**4**) with some dichlorosilano reagents produced 5-chloromethyl- (**2b**),[8,10] 5-vinyl- (**2c**),[8,10] and 5-phenyl- (**2d**)[8,10] 5-methyl-5-silacyclotriveratrylenes in the yields of 43, 40, and 23%, respectively. On the basis of ^{1}H-nmr spectra, those sila-heterocycles (**2b**, **2c**, and **2d**) should be also flexible molecules.

Construction of other metal-containing cyclophanes could be engaged by this methodology.

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7. The bromide (**3**) was practically prepared in 75% yield by reaction of 6-bromoveratryl alcohol (2 eq.) with veratrole (1 eq.) in the presence of concentrated sulfuric acid.
8. All new compounds described in the text gave satisfactory mass spectral and microanalytical data.
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10. **2b**: mp 141°C. ^{1}H-Nmr δ 0.70 (3H, s, SiMe), 3.23 (2H, s, $SiCH_2Cl$), 3.76 (6H, s, 2xOMe), 3.89 (12H, s, 4xOMe), 6.61, 6.73, 7.09 (each 2H, s, ArH); **2c**: mp 68°C. ^{1}H-Nmr δ 0.67 (3H, s, SiMe), 3.76, 3.87, 3.90 (each 6H, s, 2xOMe), 6.61, 6.74, 7.00 (each 2H, s, ArH); **2d**: mp 85°C. ^{1}H-Nmr δ 0.85 (3H, s, SiMe), 3.70, 3.77, 3.90 (each 6H, s, 2xOMe), 6.68, 6.80, 6.88 (each 2H, s, ArH); **6**: mp 236-237°C. ^{1}H-Nmr δ 0.49 (6H, s, $SiMe_2$), 3.80 (4H, bs, $2xCH_2$), 5.84 (4H, s, $2xOCH_2O$), 5.88 (2H, s, OCH_2O), 6.60, 6.68, 6.96 (each 2H, s, ArH).

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