

Development of a Sila-Friedel–Crafts Reaction and Its Application to the Synthesis of Dibenzosilole Derivatives

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Silole-based π -electron systems are currently receiving much attention as new organic optical materials because of their low-lying LUMOs,¹ and π -extended silole derivatives involving spiro-type² and ladder-type³ molecules have desirable properties, such as high fluorescence quantum yields and high glass-transition temperatures. Because of these advantages, further extension or modification of the silole framework is intriguing. However, these compounds are considered difficult to synthesize using conventional methods. Therefore, a new synthetic methodology for siloles is required, and the development of transition-metal-catalyzed [2 + 2] cyclization,^{3a} the addition of a silyl group to an alkyne,⁴ and the cross-coupling reaction of silicon-bridged biaryls have been reported recently.⁵ Despite the recent remarkable progress in this field, synthesizable silicon-containing π -conjugated skeletons are limited to benzo- or dibenzo-fused siloles, silicon-bridged stilbenes, and at most one-dimensionally extended ladder-type silafluorenes. The development of a new type of synthetic methodology will be a keystone for the further progression to two-dimensionally extended derivatives. As a new promising method, we propose the direct silylation of an aromatic ring.

The Friedel–Crafts reaction is a well-known method for the direct substitution of an aromatic ring. On the other hand, the sila-Friedel–Crafts reaction, i.e., Friedel–Crafts-type silylation involving a silenium ion^{6,7} as an intermediate, occurs only with electron-rich aromatic rings such as a ferrocene and a pyrrole.⁸ However, in the case of a nonactivated aromatic ring such as benzene, the conversion of the reaction markedly decreases.⁹ Thus, the sila-Friedel–Crafts reaction has not been used as a versatile synthetic method to date. Herein, we describe the development of an intramolecular sila-Friedel–Crafts reaction that is applicable to the synthesis of dibenzosilole derivatives. Furthermore, we have succeeded in synthesizing trisilasumanene (Chart 1), a silicon analogue of sumanene,¹⁰ by application of this sila-Friedel–Crafts reaction.

The basic strategy of the sila-Friedel–Crafts reaction for the construction of a dibenzosilole framework is shown in Scheme 1. The reaction of a hydrosilane with a trityl cation is a useful method for the generation of a silenium ion, which should spontaneously form the arene complex.¹¹ The dibenzosilole would be obtained by deprotonation from this species. The presence of a base is necessary in this reaction to prevent the reverse reaction from occurring.

Scheme 1. Strategy for the Intramolecular Sila-Friedel–Crafts Reaction

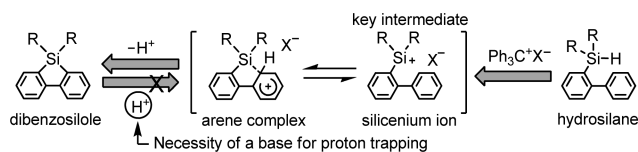
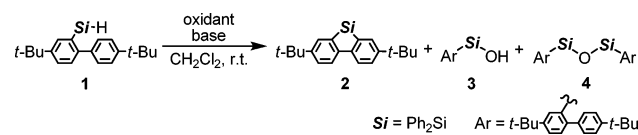


Table 1. Intramolecular Sila-Friedel–Crafts Reaction



entry	oxidant	base	% yield ^a			
			1	2	3	4
1	Ph ₃ CClO ₄	2,6-lutidine	0	52	23	25
2	Ph ₃ CB(C ₆ F ₅) ₄	2,6-lutidine	0	84	12	4
3	Ph ₃ CB(C ₆ F ₅) ₄	proton sponge	100	0	0	0
4	Ph ₃ CB(C ₆ F ₅) ₄	pyridine	— ^b	—	—	—
5	Ph ₃ CB(C ₆ F ₅) ₄	DTBMP ^c	100	0	0	0
6 ^d	Ph ₃ CB(C ₆ F ₅) ₄	diisopropylethylamine	50	0	0	0

^a Estimated by ¹H NMR. ^b A complex mixture was obtained. ^c DTBMP = 2,6-di-*tert*-butyl-4-methylpyridine. ^d An unidentified compound was generated.

The reaction of hydrosilane **1** with trityl perchlorate and 2,6-lutidine in dichloromethane at room temperature gave dibenzosilole **2** in 52% yield. Silanol **3** and disiloxane **4** were also formed as side products (Table 1, entry 1).¹² This moderate conversion may be due to deactivation of the intermediate by coordination of a perchlorate anion to the silenium ion. Changing the counteranion to tetrakis(pentafluorophenyl)borate significantly increased the conversion yield of **2** to 84% (entry 2). This reaction was very sensitive to the choice of base, and no bases other than 2,6-lutidine worked well (entries 3–6). The reasons for the high efficiency of 2,6-lutidine are still unclear, but the bulkiness and basicity of 2,6-lutidine should be important factors in this reaction.

As described above, the intramolecular sila-Friedel–Crafts reaction afforded a dibenzosilole in a good yield under mild conditions. Therefore, we applied this reaction to the synthesis of π -extended dibenzosilole derivatives. The intramolecular sila-Friedel–Crafts reaction of 2,2′-bis(diphenylsilyl)-1,1′:4′,1′′-terphenyl **5** afforded the corresponding ladder-type silafluorene **6** (Scheme 2). This result suggests that the sila-Friedel–Crafts reaction is applicable to intramolecular double cyclization.

Trisilasumanene has attracted much attention as both a sumanene analogue¹³ and a novel π -extended silole derivative.¹⁴ However, trisilasumanene is considered difficult to synthesize using conventional methods. Thus, we applied the intramolecular sila-Friedel–Crafts reaction to the synthesis of trisilasumanene. Starting

Scheme 2. Synthesis of Ladder-Type Silafluorene **6** Utilizing the Intramolecular Sila-Friedel–Crafts Reaction

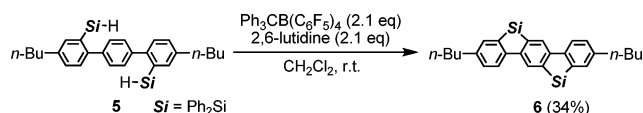
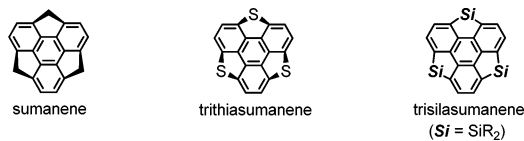
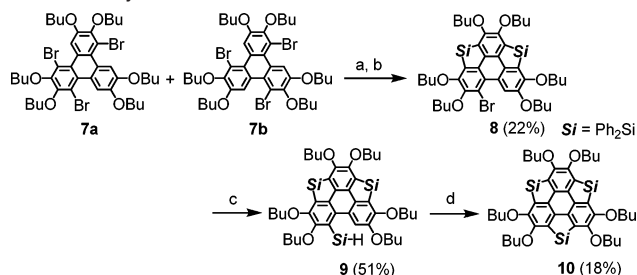


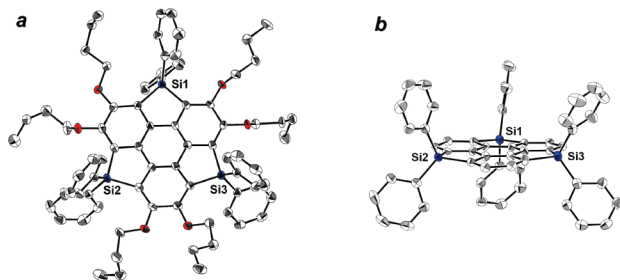
Chart 1. Structures of Sumanene and Its Main-Group Analogues, Trithiasumanene and Trisilasumanene

from an isomeric mixture of tribromotriphenylene **7**, doubly cyclized monobromide **8** was synthesized in two steps, including a dual sila-Friedel–Crafts reaction (Scheme 3). Transformation to the precursor **9** was achieved by lithiation of **8** followed by the addition of diphenylsilane in 51% yield. Finally, the intramolecular sila-Friedel–Crafts reaction was applied again to **9**, and trisilasumanene **10** was obtained in 18% yield as a colorless solid. We succeeded in X-ray crystallographic analysis of **10**. The unit cell consists of two crystallographically independent molecules that have almost the same structure; one is shown in Figure 1. It is known that sumanene and its sulfur analogue, trithiasumanene, have a bowl-shaped structure with bowl depths of 1.11 and 0.65 Å, respectively.^{15,16} The difference between the bowl depths is attributed to the larger covalent radius of the sulfur atom. X-ray structural analysis of trisilasumanene **10** indicated that the main framework was almost planar. This result is consistent with the theoretical calculations reported by Priyakumar and Sastry.¹⁴

To elucidate the electronic structure, the UV–vis absorption spectrum of trisilasumanene **10** was measured in dichloromethane (Figure S1 in the Supporting Information). An intense absorption band of **10** ($\lambda_{\text{max}} = 299$ nm, $\log \epsilon = 4.67$) was slightly red-shifted from that of 2,3,6,7,10,11-hexabutoxytriphenylene **11** ($\lambda_{\text{max}} = 280$ nm, $\log \epsilon = 5.09$) and sumanene ($\lambda_{\text{max}} = 278$ nm).¹⁷ In addition,

Scheme 3. Synthesis of Trisilasumanene **10**^a

^a (a) (i) *n*-BuLi (2.0 equiv), THF, -78°C , (ii) Ph₂SiCl₂, r.t., (iii) LiAlH₄, reflux; (b) Ph₃CB(C₆F₅)₄, 2,6-lutidine, CH₂Cl₂, r.t.; (c) (i) *t*-BuLi (2.0 equiv), Et₂O, -78°C , (ii) Ph₂SiH₂, reflux; (d) Ph₃CB(C₆F₅)₄, 2,6-lutidine, CH₂Cl₂, r.t.

**Figure 1.** (a) Top view and (b) side view of the crystal structure of trisilasumanene **10**. In (b), the six butoxy groups have been omitted for the sake of clarity.

a weak absorption band was observed in the longer-wavelength region (>350 nm) in **10**. This longer-wavelength absorption was mainly attributed to the HOMO–LUMO transition of **10** and suggested the existence of $\sigma^*-\pi^*$ conjugation on the silicon atoms. In the emission spectrum (Figure S2 in the Supporting Information), **10** showed a blue fluorescence in dichloromethane solution ($\lambda_{\text{max}} = 427$ nm) and in the solid state ($\lambda_{\text{max}} = 447$ nm).

In conclusion, we have succeeded in developing an intramolecular sila-Friedel–Crafts reaction as a novel synthetic method for dibenzosilole derivatives. This reaction proceeds under mild conditions to afford the target in a relatively high yield, indicating its availability as a versatile synthetic method. Using the intramolecular sila-Friedel–Crafts reaction, we have achieved the syntheses of a ladder-type silafluorene and trisilasumanene, a new sumanene analogue.

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Supporting Information Available: Experimental procedures, spectroscopic data for new compounds, optical properties of **10** and **11**, and a CIF file for **10**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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