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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-type[2] and ladder-type[3] 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 + 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 silicenium 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 silicenium 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

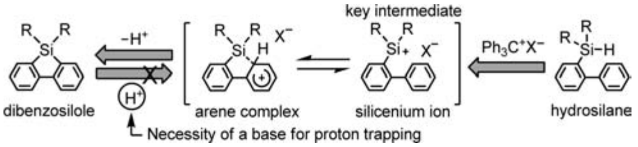
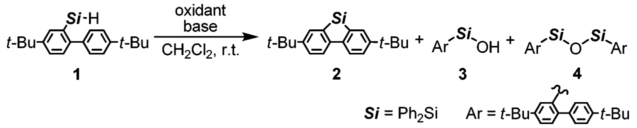


Table 1. Intramolecular Sila-Friedel−Crafts Reaction



entry	oxidant	base	% yield[a] 1	2	3	4
1	Ph_3CClO_4	2,6-lutidine	0	52	23	25
2	$Ph_3CB(C_6F_5)_4$	2,6-lutidine	0	84	12	4
3	$Ph_3CB(C_6F_5)_4$	proton sponge	100	0	0	0
4	$Ph_3CB(C_6F_5)_4$	pyridine		—[b]		
5	$Ph_3CB(C_6F_5)_4$	DTBMP[c]	100	0	0	0
6[d]	$Ph_3CB(C_6F_5)_4$	diisopropylethylamine	50	0	0	0

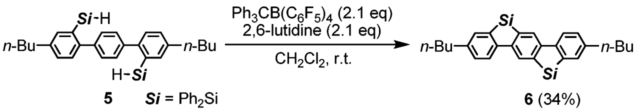
[a] Estimated by ^{1}H NMR. [b] A complex mixture was obtained. [c] DTBMP = 2,6-di-*tert*-butyl-4-methylpyridine. [d] An unidentified compound was generated.

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 silicenium 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.

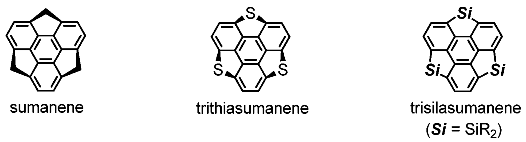
Trisilasumanene has attracted much attention as both a sumanene analogue[13] and a novel π-extended silole derivative.[14] However, trisilasumanene is considered difficult to synthesize using conventional methods. Thus, we applied the intramolecular sila-Friedel−Crafts reaction to the synthesis of trisilasumanene. Starting

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



10.1021/ja906566r CCC: $40.75

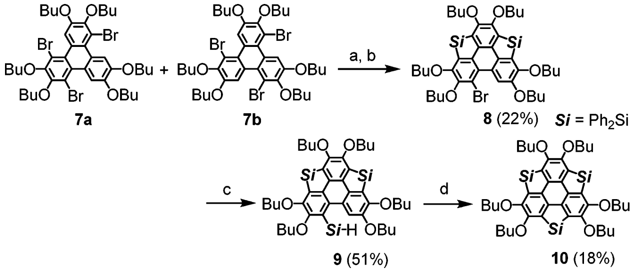
Chart 1. Structures of Sumanene and Its Main-Group Analogues, Trithiasumanene and Trisilasumanene



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** (λ_{max} = 299 nm, log ε = 4.67) was slightly red-shifted from that of 2,3,6,7,10,11-hexabutoxytriphenylene **11** (λ_{max} = 280 nm, log ε = 5.09) and sumanene (λ_{max} = 278 nm).[17] In addition, 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 (λ_{max} = 427 nm) and in the solid state (λ_{max} = 447 nm).

Scheme 3. Synthesis of Trisilasumanene **10**[a]



[a] (a) (i) *n*-BuLi (2.0 equiv), THF, −78 °C, (ii) Ph$_2$SiCl$_2$, r.t., (iii) LiAlH$_4$, reflux; (b) Ph$_3$CB(C$_6$F$_5$)$_4$, 2,6-lutidine, CH$_2$Cl$_2$, r.t.; (c) (i) *t*-BuLi (2.0 equiv), Et$_2$O, −78 °C, (ii) Ph$_2$SiH$_2$, reflux; (d) Ph$_3$CB(C$_6$F$_5$)$_4$, 2,6-lutidine, CH$_2$Cl$_2$, r.t.

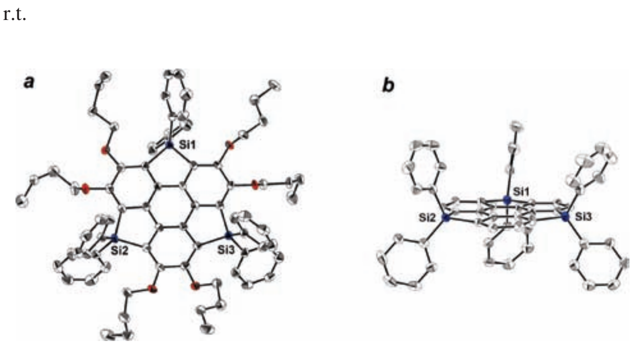


Figure 1. (a) Top view and (b) side view of the crystal structure of trisilasumanene **10**. In (b), the six butoxy groups have been omitted for the sake of clarity.

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.

References

(1) (a) Tamao, K.; Uchida, M.; Izumizawa, I.; Furukawa, K.; Yamaguchi, S. *J. Am. Chem. Soc.* **1996**, *118*, 11974. (b) Yamaguchi, S.; Tamao, K. *Chem. Lett.* **2005**, *34*, 2. (c) Wang, F.; Luo, J.; Yang, K.; Chen, J.; Huang, F.; Cao, Y. *Macromolecules* **2005**, *38*, 2253.
(2) (a) Lee, S. H.; Jang, B.-B.; Kafafi, Z. H. *J. Am. Chem. Soc.* **2005**, *127*, 9071. (b) Yang, G. C.; Su, Z. M.; Qin, C. S. *J. Phys. Chem. A* **2006**, *110*, 4817. (c) Sun, M.; Niu, B.; Zhang, J. P. *Theor. Chem. Acc.* **2008**, *119*, 489.
(3) (a) Matsuda, T.; Kadowaki, S.; Goya, T.; Murakami, M. *Org. Lett.* **2007**, *9*, 133. (b) Li, L.; Xiang, J.; Xu, C. *Org. Lett.* **2007**, *9*, 4877.
(4) (a) Ilies, L.; Tsuji, H.; Sato, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 4240. (b) Yamaguchi, S.; Xu, C.; Tamao, K. *J. Am. Chem. Soc.* **2003**, *125*, 13662. (c) Xu, C.; Wakamiya, A.; Yamaguchi, S. *Org. Lett.* **2004**, *6*, 3707. (d) Yamaguchi, S.; Xu, C.; Yamada, H.; Wakamiya, A. *J. Organomet. Chem.* **2005**, *690*, 5365. (e) Li, C.; Qiu, H.; Xu, C. *Chin. Chem. Lett.* **2007**, *18*, 1436.
(5) Shimizu, M.; Mochida, K.; Hiyama, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 9760.
(6) Recent reviews on silicenium ions: (a) Lee, V. Ya.; Sekiguchi, A. *Acc. Chem. Res.* **2007**, *40*, 410. (b) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 325.
(7) Reactions using silicenium ions: (a) Parks, D. J.; Piers, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 9440. (b) Blackwell, J. M.; Foster, K. L.; Beck, V. H.; Piers, W. E. *J. Org. Chem.* **1999**, *64*, 4887. (c) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090.
(8) (a) Sollott, G. P.; Peterson, W. R. *J. Am. Chem. Soc.* **1967**, *89*, 5054. (b) Simchen, G.; Frick, U. *Synthesis* **1984**, 929.
(9) Olah, G. A.; Bach, T.; Prakash, G. K. S. *J. Org. Chem.* **1989**, *54*, 3770.
(10) Sakurai, H.; Daiko, T.; Hirao, T. *Science* **2003**, *301*, 1878.
(11) For example, see: (a) Corey, J. Y. *J. Am. Chem. Soc.* **1975**, *97*, 3237. (b) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, *260*, 1917. (c) Lambert, J. B.; Zhao, Y.; Zhang, S. M. *J. Phys. Org. Chem.* **2001**, *14*, 370. (d) Duttwyler, S.; Zhang, Y.; Linden, A.; Reed, C. A.; Baldridge, K. K.; Siegel, J. S. *Angew. Chem., Int. Ed.* **2009**, *48*, 3787.
(12) Formation of silanol **3** and disiloxane **4** may result from trace amounts of water.
(13) Tanikawa, T.; Saito, M. *Abstr. Pap.—Chem. Soc. Jpn.* **2009**, *89*, 1E1-04.
(14) (a) Priyakumar, U. D.; Sastry, G. N. *J. Org. Chem.* **2001**, *66*, 6523. (b) Priyakumar, U. D.; Punnagai, M.; Mohan, G. P. K.; Sastry, G. N. *Tetrahedron* **2004**, *60*, 3037.
(15) Sakurai, H.; Daiko, T.; Sakane, H.; Amaya, T.; Hirao, T. *J. Am. Chem. Soc.* **2005**, *127*, 11580.
(16) Imamura, K.; Takimiya, K.; Aso, Y.; Otsubo, T. *Chem. Commun.* **1999**, 1859.
(17) Amaya, T.; Mori, K.; Wu, H.-L.; Ishida, S.; Nakamura, J.; Murata, K.; Hirao, T. *Chem. Commun.* **2007**, 1902.

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