

Modular Synthesis of Functionalized Benzosiloles by Tin-Mediated Cyclization of (*o*-Alkynylphenyl)silaneLaurean Ilies,[†] Hayato Tsuji,^{*,†} Yoshiharu Sato,[‡] and Eiichi Nakamura^{*,†,‡}

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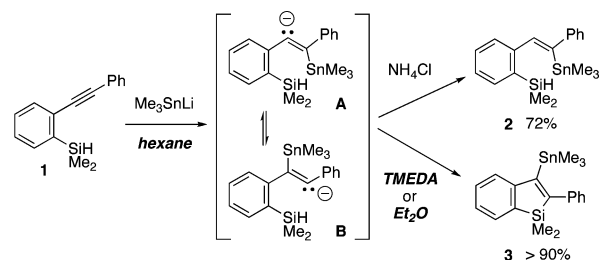
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Efficiency and diversity are central concepts in modern organic synthesis. It is in this context that modular synthesis and molecular libraries have attracted much interest in the design of functional materials. We have been exploring for some time the potential of this approach¹ and have discovered a new class of hole-transporting materials in our studies on 3-metallobenzofuran modules.² We report herein the synthesis of a variety of silole derivatives, based on a new cyclization reaction of (*o*-alkynylphenyl)silane **1** and derivatization of the resulting 3-stannylbenzosilole **3** (Scheme 1). This stannane derivative **3** serves either as a useful nucleophilic unit by itself or as an electrophilic unit after conversion into the corresponding iodide **10** (eq 2). We have synthesized a variety of benzosilole derivatives, including a new phenylene-bis(benzosilole) **9** (Table 2), which exhibits the highest electron drift mobility³ among known silole derivatives⁴ or commonly used electron transporting materials (ETM).

Despite the rich history of the synthesis of siloles,^{5–7} the concept of diversity synthesis has been lacking in this field, and we envisioned that an organometallic unit, such as **3**, would become a useful synthetic tool. In analogy to our recent benzoheterole synthesis,^{1a,b} we considered that anionic or cationic activation of the silane moiety in the (*o*-alkynylphenyl)silane **1** would form the desired silole ring. However, all attempts to achieve such cyclization failed. Among our final attempts, we tried the reaction shown in Scheme 1 and found that a high yield of the desired product **3** occurs when the reaction is carried out in diethyl ether. This was a surprise for two reasons. First, there was a report that Et₃SnLi in THF adds to diphenylacetylene only in 2% yield.⁸ Second, while the successful cyclization implies the formation of an intermediate **B** instead of the less hindered one **A**, the same reaction in hexane suggested the intermediacy of **A**. Thus, the reaction in hexane instead of diethyl ether gave **2** after quenching with aqueous NH₄Cl. More interestingly, the reaction in hexane also produced **3**, when diethyl ether or *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was added before aqueous quenching. Clearly, the reaction is highly sensitive to the solvent.⁹ The results suggest that **A** and **B** interconvert with each other under certain reaction conditions. Note that the displacement of a hydride by a vinyl lithium that occurs on the way from **B** to **3** is a known reaction.¹⁰

The cyclization reaction took place not only with stannyl lithium reagents but also with silyllithium reagents as summarized in Table 1. The Me₃SnLi-promoted reaction on a 1 mmol scale proceeded in 93% yield (Table 1, entry 1) and, on a 20 mmol scale, gave 90% yield to afford 7.15 g of **3**. Bu₃SnLi gave a lower yield of the cyclized product (entry 2). A triorganosilyllithium reagent¹¹

Scheme 1

Table 1. Metalative Cyclization of **1** into Benzosilole **3**^a

entry	reagent	conditions ^b	3 (%) ^c	1 (%) ^d
1	Me ₃ SnLi	Et ₂ O, rt, 3 h	93	2
2	Bu ₃ SnLi	Et ₂ O, 0 °C, 21 h	64	13
3	PhMe ₂ SiLi	THF, 0 °C, 1 h	13 ^d	60
4	(Et ₂ N)Ph ₂ SiLi	THF, 0 °C, 3 h	87 ^d	0

^a Details of the reaction conditions are described in the Supporting Information. The reaction can be applicable to the synthesis of 2-arylbenzosiloles other than the 2-phenyl compound **3** (data not shown). ^b Optimized for each reagent. ^c Isolated yield. ^d Determined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

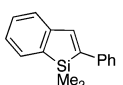

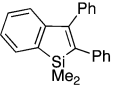

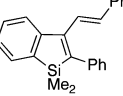

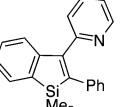

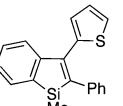
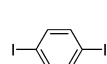
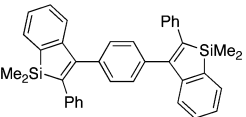
in THF also produced the desired 3-silylbenzosilole, and an aminosilyllithium¹² gave a much higher yield of the product (entries 3 and 4).

First we examined the nucleophilic reactivity of **3** under Kosugi-Migita-Stille cross-coupling conditions. The reaction with iodobenzene in the presence of Pd₂dba₃·CHCl₃, P(*t*-Bu)₃, and CsF in 1,2-dimethoxyethane¹³ gave 2,3-diphenylbenzosilole **5** in 63% yield (Table 2, entry 2 in the parentheses). When the tin atom was first transmetalated to lithium¹⁴ and then to zinc, the efficiency of the cross-coupling improved considerably (Table 2, eq 1). Thus, **3** was first quantitatively converted to 3-lithiobenzosilole upon treatment with BuLi at 0 °C in THF, as proved by the ammonium chloride quenching (entry 1). Subsequent transmetalation with zinc chloride, followed by Negishi cross-coupling with iodobenzene in the presence of Pd₂dba₃·CHCl₃ and dicyclohexyl(2',6'-dimethoxybiphen-2-yl)phosphine **L**¹⁵ in THF/NMP gave the desired 2,3-difunctionalized benzosilole **5** in 87% isolated yield (entry 2). Styryl bromide and 2-pyridyl bromide also reacted smoothly and gave the corresponding benzosiloles **6** and **7** in 90% and 91% yield, respectively (entries 3 and 4). 2-Thienyl bromide gave the corresponding benzosilole **8** in 53% yield (entry 5). The efficiency of the modular approach is illustrated by the one-pot synthesis of the phenylene-bridged bis(benzosilole) **9**, which was achieved in 84% yield (entry 6).

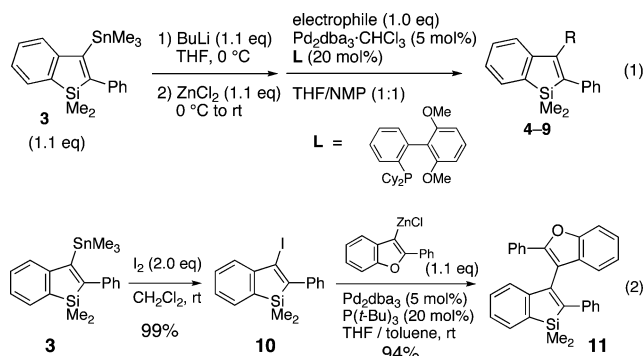
We can also use the benzosilole unit in **3** as an electrophile (eq 2). We thus treated **3** first with iodine to obtain the iodide **10** and then with a 3-zincbenzofuran that was obtained by cyclization

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Table 2. Functionalization of **3** with Various Electrophiles^a

entry	electrophile	product	yield (%) ^b
1	H ⁺		97 ^c
2			87 (63) ^d
3			90
4			91
5			53
6			84

^a Reaction conditions are summarized in eq 1.¹⁶ ^b Isolated yield based on the halide. ^c The reaction mixture was quenched with aqueous ammonium chloride after destannylation. ^d The reaction was carried out under Kosugi-Migita-Stille cross-coupling conditions.



of the oxo-analog of **1**, as previously described.^{1b} This two-step sequence took place with excellent overall yield to give the silole/benzofuran compound **11**. In light of the electron-transporting property of silole and the hole-transporting ability of benzofuran derivatives,² we expect that this synthetic approach will provide a new access to ambipolar organic semiconductors.

To examine the utility of the modular approach in the design of organic materials, we examined the physicoelectronic properties of the phenylene-bridged bis(benzosilole) **9**. Upon recrystallization from hexane and chloroform, **9** gave single crystals. The molecule is nonplanar, as steric repulsion tilts the benzosilole moieties out of the central benzene plane.¹⁶ After fast cooling, the melt of **9** yielded a glassy solid. Differential scanning calorimetry (DSC) analysis of the sample indicated a glass transition at 66 °C and crystallization at 126 °C.¹⁶ The electron affinity of the amorphous solid of **9** was 2.70 eV, as calculated from the ionization potential obtained by photoemission yield spectroscopy and the optical gap

inferred from the absorption spectrum of the film. The electron drift mobility was found to be very high, 6×10^{-4} cm²/Vs, which is higher than that of all previously reported silole-based materials or that of the most widely used ETM, tris(8-hydroxyquinolinolato)-aluminum(III) (Alq₃).^{4a} This mobility measurement was performed by the time-of-flight technique using an amorphous film made by vacuum deposition (thickness: 3.59 μm) at room temperature in an electric field of 4.5×10^5 V/cm. The amorphous character of the film was confirmed by XRD.¹⁶

In conclusion, we discovered a mechanistically intriguing stannylation or silylation cyclization reaction of (*o*-alkynylphenyl)silane **1** that gives a stable 3-stannyl or 3-silylbenzosilole. The stannyl compound **3** and the corresponding iodo compound **10** can then be used as useful modules for quick construction of a variety of previously inaccessible benzosilole derivatives including the electron-transporting bis(benzosilole) **9**. The versatility of this modular approach will allow us to obtain a variety of silole derivatives, and we expect that useful organic semiconductors and materials for electroluminescent devices or solar cells can be discovered using such a molecular library.

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Supporting Information Available: Detailed experimental procedures and properties of the compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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