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Synthesis of Benzo[*b*]siloles via KH-Promoted Cyclization of (2-Alkynylphenyl)silanes

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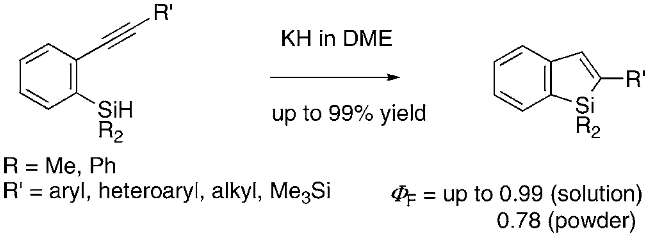
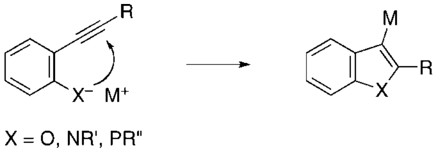
ABSTRACT



(2-Alkynylphenyl)silanes undergo intramolecular cyclization in the presence of an excess or a subequimolar amount of potassium hydride to give a variety of new 2-substituted benzosiloles in good to excellent yields. Some of these compounds showed a high fluorescence quantum yield both in solution and in the solid state, and they also showed reversible reduction in THF.

The importance of benzoheteroles such as indole has long been established in biology-related chemistry including medicinal chemistry; however, their importance for materials science has been grossly underestimated. We have focused for some time on possible applications of benzoheteroles in optoelectronic devices and synthesized nitrogen-, oxygen-, and phosphorus-containing derivatives.[1] We also demonstrated their applications as efficient materials for organic light-emitting diode (OLED) devices, both in a multilayered (heterojunction) architecture and in a device utilizing a single organic compound (homojunction).[2] Our synthetic routes to benzoheteroles employed the cyclization strategy outlined in eq 1, where a heteroatom anion adds intramolecularly to a triple bond to form a 3-metallobenzoheterole.



(1)

This scheme, however, could not be applied to benzosiloles, probably because of the unfavorable polarity of the Si−H bond in **1**,[3] and this failure forced us to resort to a more complicated, tin-based route.[4] The good *n*-type semiconducting properties of the benzosiloles thus obtained prompted us to reinvestigate the base-promoted cyclization route. In this paper, we report a cyclization reaction of an alkynylsilane **1** that gives a variety of 2-substituted benzosiloles **2** in high yields in the presence of an essentially catalytic amount of KH (Scheme 1). The new compounds add to the repertoire of siloles,[5] many of which are known for their high electron-transporting ability[6] and enhanced luminescence in the solid state.[7]

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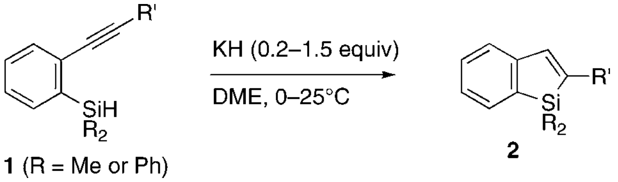
10.1021/ol9015282 CCC: $40.75

Scheme 1. Cyclization of (2-Alkynylphenyl)silane **1** to 2-Substituted Benzosilole **2**



A variety of conditions that would generate a dimethylsilyl anion from **1** (R = Me) failed to give **2** in a synthetically significant yield.[8] Following a report by Corriu, who suggested the formation of the desired silyl anion by the reaction of a hydrosilane with KH,[9] we found that 0.2−1.5 equiv of KH in 1,2-dimethoxyethane (DME) promotes formation of **2a** in up to 70% yield (Table 1, entries 1 and 2). Consistently high yields were obtained when reagent-grade DME without further purification was used as a solvent, or when the reaction was carried out in the open air or in the presence of excess or a subequimolar amount of KH.[10] However, ethereal solvents other than DME dramatically decreased the yield.[11]

Table 1. KH-Promoted Cyclization of (2-Alkynylphenyl)silane **1** to 2-Substituted Benzosilole **2**[a]

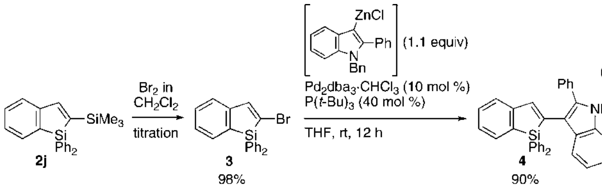
entry	R′	R	2	conditions	yield[b] (%)
1	phenyl	Me	**2a**	25 °C, 3 h	70
2	phenyl	Me	**2a**	25 °C, 4 h[c]	61[d]
3	4-biphenyl	Me	**2b**	25 °C, 3 h	71
4	phenyl	Ph	**2c**	0 °C, 0.5 h	90
5	1-naphthyl	Ph	**2d**	0 °C, 2 h	99
6	4-$CF_3C_6H_4$	Ph	**2e**	0 °C, 0.5 h	93
7	4-$MeOC_6H_4$	Ph	**2f**	25 °C, 1 h	97
8	2-pyridyl	Ph	**2g**	0 °C, 1 h	81
9	2-thienyl	Ph	**2h**	0 °C, 0.5 h	60
10	(*E*)-styryl	Ph	**2i**	0 °C, 1 h	92
11	$SiMe_3$	Ph	**2j**	0 °C, 2 h	98
12	butyl	Ph	**2k**	25 °C, 16 h	46[d]

[a] Reaction of **1** with ca. 1 equiv of KH in DME under the indicated conditions. See the Supporting Information for details. [b] Isolated yield. [c] 0.2 equiv of KH was used. [d] Determined by ^{1}H NMR in the presence of 1,1,2,2-tetrachloroethane as an internal standard.

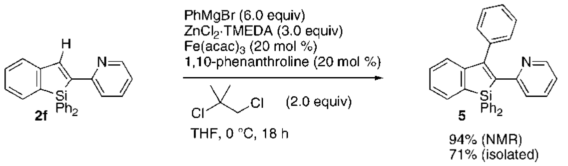
The reaction of the diphenylsilyl compound **1** (R = Ph) was much faster and higher yielding (entry 4), presumably because of the faster generation of a reactive silicon intermediate. The cyclization of **1** (R = Ph) bearing a variety of R′ substituents on the alkyne moiety (entries 5−12) showed that the reaction is very general. A sterically demanding 1-naphthyl group did not hinder the reaction at all to give **2d** in quantitative yield (entry 5). Both electron-poor and electron-rich substrates reacted well, as exemplified by the synthesis of 4-CF_3- and 4-MeO-phenylbenzosiloles **2e** and **2f** in excellent yields (entries 6 and 7). Benzosiloles bearing a 2-pyridyl (**2g**) and a 2-thienyl (**2h**) group could also be synthesized (entries 8 and 9). An enyne substrate reacted with retention of the double-bond geometry to give a conjugated benzosilole **2i** in excellent yield (entry 10). The substrate possessing a trimethylsilyl group also cyclized to obtain **2j** in excellent yield (entry 11), whereas a substrate possessing an aliphatic group gave **2k** in moderate yield, together with recovered starting material (entry 12).

The 2-substituted benzosiloles can be further functionalized. For example, 2-trimethylsilylbenzosilole (**2j**) was converted first to a 2-bromobenzosilole (**3**) and then coupled with 3-zincioindole[1b] in the presence of Pd(0) catalyst[12] to obtain a mixed heterocyclic compound **4** in high yield (eq 2).

An Fe-catalyzed C−H bond activation reaction that we recently reported[13] can introduce an aryl group in the C3 position of the 2-pyridylbenzosilole (**2g**, eq 3). Thus, **2g** was coupled with a phenylzinc reagent in the presence of $Fe(acac)_3$ (20 mol %), 1,10-phenanthroline (20 mol %), and 1,2-dichloroisobutane (2.0 equiv) to obtain the expected 2-phenyl-3-pyridylbenzosilole (**5**) in excellent yield.[14]



(2)



(3)

The crystal structure of **2b** (Figure 1) indicated that the 2-substituent is tilted out of the benzosilole plane by 39.4(2)°,

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(8) Organic bases such as *n*-BuLi, *t*-BuLi, Et_2Zn, and *t*-BuOK did not effect the cyclization of **1a**.

(9) (a) Corriu, R. J. P.; Guérin, C. *J. Chem. Soc., Chem. Commun.* **1980**, 168–169. (b) Corriu, R. J. P.; Guérin, C.; Kolani, B. *Bull. Soc. Chim. Fr.* **1985**, *5*, 973–979.

(10) Pretreatment of KH to remove impurities was not necessary.

(11) THF: 25% yield. Et_2O: 0% yield.

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(13) Norinder, J.; Matsumoto, A.; Yoshikai, N.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 5858–5859.

(14) Compound **5** was slightly sensitive to silica gel chromatography, leading to lower isolated yield.

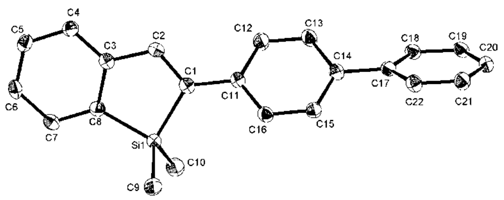

Figure 1. ORTEP drawing of 1,1-dimethyl-2-(4-biphenyl)benzosilole (**2b**) (50% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity.

and the two phenyl groups are tilted by a similar angle, 38.2(2)°. The silole−phenyl tilt angle is essentially the same as the angle previously reported for a 2,3-disubstituted benzosilole (1,4-bis(1,1-dimethyl-2-phenylbenzosilol-3-yl)-benzene, 44.41(17)°).[4]

A study of the photophysical and electrochemical properties of the new benzosiloles indicated that some compounds show high fluorescence quantum yields both in solution and in the solid state, high electron affinity, and stability under electrochemical conditions (Table 2). The series of synthesized 2-substituted compounds (Table 1) allowed a systematic study of the factors that affect the properties. All of the compounds showed absorption maxima in the 330−350 nm range and emission maxima in the blue region (390−414 nm). The solid-state emission was only slightly red-shifted (typically 10−20 nm, value given in parentheses) compared with that in solution, suggesting a lack of strong intermolecular interactions in the solid state.

Table 2. Summary of the Photophysical and Electrochemical Properties of Functionalized Benzosiloles

cmpd	$\lambda_{abs}{}^{a}$ (nm)	$\epsilon \times 10^{-4}$ (L mol^{-1}cm^{-1})	$\lambda_{em}{}^{a,b}$ (nm)	$\Phi_F{}^{b,c}$	$E_{1/2}{}^{d}$ (V)
2a	333	1.5	390 (406)	0.55 (0.46)	-2.82^{e}
2c	338	1.3	400 (410)	0.91 (0.78)	−2.61
2e	336	1.4	401 (422)	0.26 (0.77)	-2.41^{e}
2f	350	1.6	418 (437)	0.99 (0.72)	−2.75
2g	339	1.4	395 (422)	0.41 (0.70)	−2.49
5	339	1.6	406 (428)	0.004 (0.52)	−2.49

[a] In dichloromethane. [b] Irradiated at 300 nm. Value in parentheses for the solid-state measurement. [c] Absolute quantum yield determined by a calibrated integrating sphere system. [d] Reduction half-wave potential determined by CV for a THF solution (0.5 mmol/L), using TBAP (0.1 mol/L) as an electrolyte. The values are corrected from a ferrocene standard. The scan rate was 100 mV/s. Glassy carbon was used as the working electrode, platinum wire was used as the counter electrode, and Ag^+/Ag was used as a standard electrode. [e] Reduction potential for an irreversible wave, determined by DPV and corrected from ferrocene.

The absolute fluorescence quantum yield of a dichloromethane solution of benzosiloles **2** showed strong dependence on the substituents. Changing the substituent on the silicon atom from methyl (**2a**) to phenyl (**2c**) resulted in a significant increase in quantum yield, presumably because of the smaller rotational freedom in the latter. The electron density of the 2-substituent appears to affect the quantum yield in solution (for example, 0.26 for **2e** and 0.99 for **2f**), while in the solid state, this effect was leveled (for example, 0.77 for **2e** and 0.72 for **2f**). The fluorescence quantum yield of 2,3-disubstituted compound **5** in solution was very low, while it was enhanced by more than 100-fold in the solid state.[7] This is an attractive feature when we consider the application of this class of compounds as emissive materials in OLED devices.[15]

Increased electrochemical stability and lower reduction potential were observed upon changing the 1-substituent from the dimethyl to the diphenyl group (**2c** vs **2a**). As expected, the 2-substituent affected the electrochemical properties. Thus, compounds **2e** and **2g**, which possess an electron-deficient substituent, were reduced at lower potentials than those bearing a phenyl group. Interestingly, the 3-phenyl group in **5** did not affect the reduction potential, suggesting the 2-substitutent has a dominant effect on the LUMO level of a 2,3-diaryl benzosilole. We expect that the observed properties will be useful information for utilizing these *n*-type semiconductors in optoelectronic devices.[15]

In conclusion, KH promotes cyclization of (2-alkynylphenyl)silanes to 2-substituted benzosiloles, a simple and convenient reaction possessing a broad synthetic scope. While the reaction mechanism is not clear at this stage, the catalytic nature of the reaction and other indirect evidence may suggest that the reaction could take place via a pentacoordinated silicate species rather than via a discrete silyl anion as depicted in eq 1.[16] The observed physical properties of the products suggest the utility of these benzosiloles as organic electronic materials.

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Supporting Information Available: Experimental details and CIF file for compound **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) H_2 was not detected when the reaction was monitored by ^1H NMR, suggesting that rather than deprotonation, the hydride may have attacked the silane in a nucleophilic fashion, then the resulting pentacoordinated hydridosilicate intramolecularly reduced the triple bond, and finally the generated vinyl anion attacked the silicon atom to effect the cyclization together with hydride elimination. See: (a) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371–1448. (b) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17–31.