Endo–Endo Mode Intramolecular Reductive Cyclization of Cyclic 1,2-Bis(silylethynyl)benzenes

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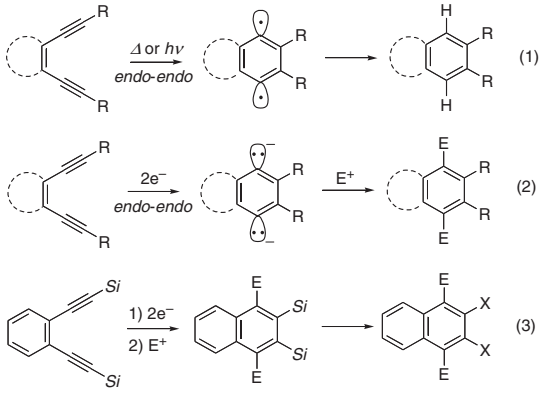
Upon treatment of cyclic 1,2-bis(silylethynyl)benzenes with lithium naphthalenide, the intramolecular reductive cyclization proceeds in an *endo–endo* mode to produce 1,4-dilithio-2,3-disilylnaphthalenes, which are transformed into a series of 1,4-difunctionalized 2,3-disilylnaphthalenes.

The Bergman cyclization is a radicallic cyclization of enediynes,[1] which proceeds in an endo–endo mode[2] to produce 1,4-dehydrobenzene biradicals (Eq 1). This reaction has attracted much attention not only from a biological viewpoint as a key action of the enediyne antibiotics,[3] but also from a recent interest in materials science as a new methodology for the construction of π-conjugated frameworks.[4] However, one synthetic drawback of this reaction is the limited scope of the functional group transformation from the 1,4-dehydrobenzene biradicals. In this regard, its anionic analogous reaction, i.e., the intramolecular reductive cyclization of the enediynes (Eq 2) would have a greater synthetic potential, since the produced ring is a dianion which can be trapped with a variety of electrophiles. However, only a few examples of this type of cyclization have been reported so far.[5–8] As a related reaction, we recently developed the endo–endo mode reductive cyclization of bis(phenylethynyl)-silanes, which is a general synthetic method for 2,5-difunctionalized siloles.[2a] To extend this methodology to the enediyne-type substrates, we investigated the reductive cyclization using 1,2-bis(silylethynyl)benzenes as the starting materials (Eq 3). We envisioned that the use of the silyl groups at the acetylene terminus would be beneficial in terms of further functional group transformation after the cyclization, which would increase the synthetic utility of this methodology.



Previous papers reported that the reductive cyclization of the enediyne-type substrates can proceed not only in the endo–endo mode but also in an exo–endo mode.[2] For instance, while the reductive cyclization of enediyne **1** affords **2** as one of the products,[6] the reaction of 1,2-bis(phenylethynyl)benzene **3** proceeds

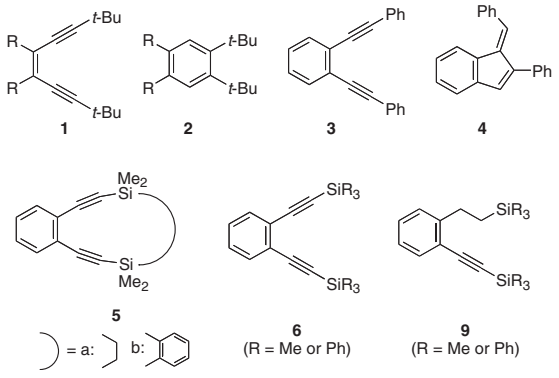
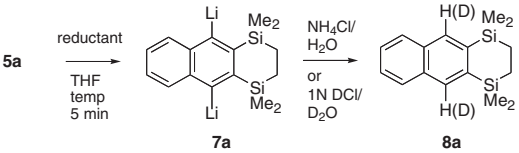


Table 1. Reduction of cyclic bis(silylethynyl)benzene **5a**



Entry	Reductant[a]	Temp.	Quenching reagents	Yield[b]
1	LiNaph (4)	rt	NH_4Cl/H_2O	65%
2	LiNaph (4)	rt	DCl/D_2O	50% (74%D)
3	LiNaph (4)	0 °C	DCl/D_2O	52% (92%D)
4	LiNaph (2.5)	0 °C	DCl/D_2O	63% (91%D)
5	LDBB (4)	−10 °C	DCl/D_2O	26% (97%D)

[a]Molar amounts of the reductants in the parentheses.
[b]Deuteriation percentage in the parentheses.

in the exo–endo mode to give **4**.[5,9] Thus, the question is how to control the reaction mode. Our strategy to answer this question is the use of the cyclic derivatives of the 1,2-bis(silylethynyl)-benzenes. Two cyclic derivatives bearing 1,2-ethylene (**5a**) and 1,2-phenylene (**5b**) tethers were prepared from 1,2-bis(trimethylsilylethynyl)benzene **6** (R = Me) by the desilyllithiation using *n*-BuLi in THF, followed by treatment with the appropriate bis(chlorosilane)s.

The results of the reaction of **5a** with reductants are summarized in Table 1. Typically, upon treatment of **5a** with 4 molar amounts of lithium naphthalenide (LiNaph) at room temperature for 5 min, followed by quenching with an NH_4Cl aqueous solution, the cyclization indeed proceeded in the endo–endo mode to give the target product **8a** in 65% yield (Entry 1). To confirm the formation of the dianion intermediate **7a**, the reaction mixture was quenched with 1N DCl/D_2O solution instead of the NH_4Cl aqueous solution; a 74%-deuteriated cyclized product was obtained when the reaction was performed at room temperature (Entry 2), suggesting that substantial hydrogen abstraction prob-

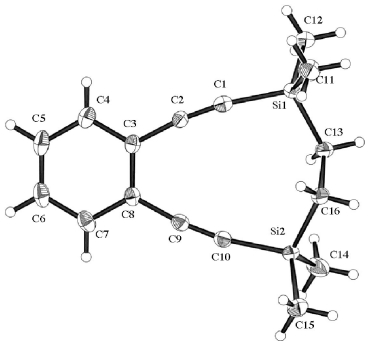
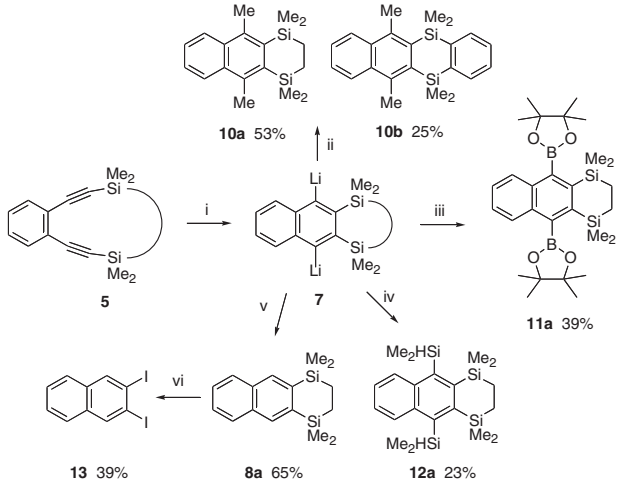


Figure 1. ORTEP drawing of **5a** (50% probability for thermal ellipsoids). Selected bond lengths [Å] and angles [deg]: Si1–C1 1.847(4), C1–C2 1.210(5), C2–C3 1.432(5), C3–C8 1.399(5), Si1–C1–C2 169.1(3), C1–C2–C3 172.6(4), C2–C3–C8 118.3(3). C1···C8 nonbonded distance, 3.63 Å.



Reagents and conditions: i, LiNaph, THF, 0 °C, 5 min; ii, $(MeO)_2SO_2$; iii, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; iv, Me_2HSiCl; v, NH_4Cl/H_2O; vi, ICl, CH_2Cl_2, rt.

Scheme 1.

ably from the solvent took place at this temperature, and the deuteriation percentage increased to 92% in the reaction at 0 °C (Entry 3). Using a stronger reductant, lithium 4,4′-di-*tert*-butylbiphenylide (LDBB), the reaction could be carried out at lower temperature (−10 °C), resulting in a higher deuteriation percentage, although the yield of the product substantially decreased (Entry 5). When the amount of the reductant was reduced to 2.5 molar amounts, no significant change was observed (Entry 4).

To elucidate the effect of the cyclic structure in the starting material, we also carried out the reactions of *acyclic* substrates **6** (R = Me or Ph) with LiNaph (4 molar amounts). Although a complex mixture was obtained at 0 °C, at the decreased temperature such as −78 °C, not the cyclization but the full reduction of one acetylene moiety occurred to produce 1-(2-silylethyl)-2-(silylethynyl)benzenes **9** as the major product (isolated yields: R = Me, 32%; R = Ph, 71%). Their structures were identified based on ^1H and ^{13}C NMR spectroscopies and by the X-ray crystallography of **9** (R = Ph).[10] These results demonstrate that a spatial proximity between the two acetylene moieties in the cyclic diethynylbenzenes is crucial to realize the *endo–endo* mode cyclization, as well established in the chemistry of the Bergman cyclization.[1] According to the crystal structure of **5a** (Figure 1)[10] and the calculated structure of **6** (R = Me, at the B3LYP/6-31G(d) level of theory), the inter-acetylenic distance at the terminal positions (**5a**, 3.63 Å; **6**, 4.20 Å) is reduced about 0.6 Å by forming the cyclic structure.

To demonstrate the synthetic utility of the present cyclization, we performed several functional group transformations, as summarized in Scheme 1. Thus, the 1,4-dilithiated naphthalene **7a** produced from **5a** was trapped with dimethyl sulfate to give the dimethylated product **10a** in 53% yield. Similarly, a benzo-analogue **10b** was obtained starting from **5b**, although the yield is low. As for the electrophiles, the use of a 2-isopropoxy-1,3,2-dioxaborolane derivative and dimethylchlorosilane afforded 1,4-diboryl-2,3-disilylnaphthalene **11a** and 1,2,3,4-tetrasilylnaphthalene **12a**, respectively. In addition, it is noteworthy that the 2,3-bis(silyl) groups can be converted into halogens by the halodesilylation, as exemplified by the transformation from **8a** to **13** using ICl. These results suggest the possible application of the present methodology for the synthesis of functionalized acenes, which have now attracted significant attention as promising materials for organic electronics.[11] Further study in this direction is currently in progress in our laboratory.

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10 Crystallographic data for **5a** and **9** have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-220820 and 220821, respectively. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/consts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Uinon Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).
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