Organic LETTERS

Letter

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Diisobutylaluminum Hydride Promoted Cyclization of 1-Hydrosilyl-4-silyl-1,3-enynes to Polysubstituted Siloles

Hidenori Kinoshita, Akihiro Ueda, Hiroki Fukumoto, and Katsukiyo Miura*

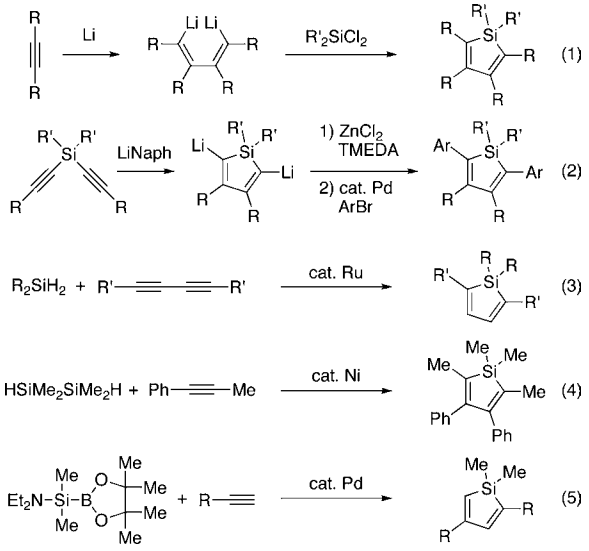
Department of Applied Chemistry, Graduate School of Science and Engineering, Saitama University, 255 Shimo-ohkubo, Sakura-ku, Saitama 338-8570, Japan

Supporting Information

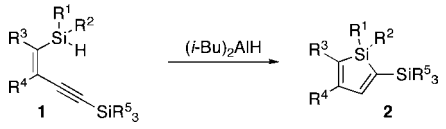
ABSTRACT: An efficient method for preparing unsymmetrically multisubstituted siloles is described. The reaction of 1-hydrosilyl-4-silyl-1,3-enynes with diisobutylaluminum hydride (DIBAL-H) gave multisubstituted siloles in good to high yields. This method could be applied to the synthesis of benzosiloles using 2-hydrosilyl-1-(silylethynyl)benzenes as substrates. The silole formation was also promoted even by a substoichiometric amount of DIBAL-H. The reaction provides a straightforward method to prepare siloles and benzosiloles.

Siloles have unique electronic and photophysical properties due to the low energy of the lowest unoccupied molecular orbitals compared with their carbon analogues.[1,2] Therefore, much attention has been focused on their use as electron-transport and light-emitting materials for organic electron devices.[3] Synthetic methods for substituted siloles have also been investigated intensively to impart more efficient properties by variations of the substituents. The conventional methods for silole synthesis are those via reductive cyclization, which provide rapid access to symmetrically substituted siloles by a successive bond-forming process (eqs 1 and 2 in Scheme 1).[4,5] Excellent approaches to substituted siloles have also been achieved by transition-metal catalysis as shown in the Ru-catalyzed double *trans*-hydrosilylation of 1,3-diynes (eq 3)[6] and the Ni- and Pd-catalyzed [2 + 2 + 1] cycloadditions using silylene equivalents (eqs 4 and 5).[7,8] Despite all of the efforts that have been made toward the efficient synthesis of siloles, the regiodefined synthesis of unsymmetrically substituted siloles bearing different substituents has largely remained unexplored. There is much room for developing new synthetic methods to extend the diversity of the potentially beneficial compounds. To address this issue, we adopted a preinstallation approach via intramolecular C−Si bond formation of linear substrates bearing desired substituents at the defined positions. We report herein that the DIBAL-H-promoted cyclization of 1-hydrosilyl-4-silyl-1,3-enynes **1** and related compounds **3** is valuable for the regiodefined synthesis of unsymmetrically substituted siloles (Scheme 2).

Scheme 1. Known Methods for Silole Synthesis



Scheme 2. DIBAL-H-Promoted Silole Synthesis

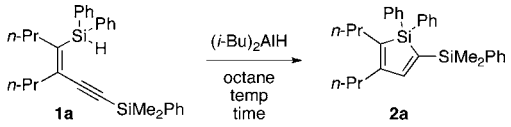


In the course of our study on synthetic uses of DIBAL-H,[9] we found that the treatment of 1,3-enyne **1a**, bearing a hydrosilane moiety, with DIBAL-H gave silole **2a** (Table 1). With this finding, our goal was set to develop a new method for silole synthesis by the DIBAL-H-promoted cyclization. We commenced the optimization of reaction conditions using **1a**, which can be accessed easily from known 1-bromo-1,3-enynes,[10] as a probe. The reaction of **1a** with 1.5 equiv of DIBAL-H at 75 °C for 24 h afforded **2a** in 64% yield (entry 1). When the isolated product **2a** was treated with DIBAL-H (1.5 equiv) under the same conditions, it was converted into a complex mixture of products. This observation implied that **2a**

Received: January 5, 2017
Published: February 1, 2017

DOI: 10.1021/acs.orglett.7b00038
Org. Lett. 2017, 19, 882−885

Table 1. Optimization of Reaction Conditions[a]



entry	DIBAL-H (equiv)	time (h)	temp (°C)	yield of **2a**[b] (%)
1	1.5	24	75	64
2	1.5	2	75	76
3	1.5	1	75	86
4	1.5	0.5	75	92
5	1.5	0.17	75	81[c] (11)[c,d]
6	1.2	0.5	75	93
7	1.0	0.5	75	91
8	0.5	0.5	75	83[c] (4)[c,d]
9	0.5	1	75	81
10	0.5	3	80	81
11	0.3	1	75	40[c] (48)[c,d]
12	0.3	2	75	63[c] (20)[c,d]
13	0.3	4	75	69[c] (13)[c,d]
14	0.3	2	80	64[c] (19)[c,d]
15	0.2	2	75	0[e]
16	0.1	2	75	0[e]
17	1.2	0.5	70	76[c] (9)[c,d]
18	1.2	0.5	80	96
19	1.2	0.5	90	84

[a]Unless otherwise noted, all reactions were carried out with **1a** (0.25 mmol) in octane (0.75 mL). [b]Isolated yield. [c]NMR yield (Bn_2O as an internal standard). [d]Recovery of **1a** in parentheses. [e]**1a** was recovered almost quantitatively.

underwent DIBAL-H-promoted side reactions during the reaction of **1a**. This is the reason that the reaction time was scrutinized (entries 2−5). The time variations revealed that the reaction was completed within 0.5 h and that **2a** was gradually decomposed as predicted. The reaction for 0.5 h achieved a 92% isolated yield of **2a** (entry 4). Then the effect of amount of DIBAL-H was investigated (entries 6−16). The cyclization using 1.2 equiv of DIBAL-H proceeded in 93% yield (entry 6). It is noteworthy that a substoichiometric amount of DIBAL-H (0.5 equiv) was enough to promote the reaction (entries 8−10), although an elongated reaction time was needed to complete the conversion of **1a**. With less than 0.5 equiv of DIBAL-H, the reaction was not completed (entries 11−16). In particular, the reaction using 0.1 or 0.2 equiv of DIBAL-H did not give **2a** at all, and an almost quantitative yield of **1a** was recovered. Finally, variations in reaction temperature were examined in the reaction with 1.2 equiv of DIBAL-H for 0.5 h (entries 17−19). As a result, **2a** was obtained in 96% isolated yield at 80 °C (entry 18).

With the optimized reaction conditions in hand, the scope of this transformation was investigated (Figure 1). Enynes **1b** and **1c**, bearing a different silyl group at the alkyne terminus, were submitted to the optimized conditions. The desired siloles **2b** and **2c** were formed in excellent yields. The larger scale reaction of **1b** (1 mmol) gave **2b** in 83% isolated yield. Enyne **1d**, bearing a dimethylsilyl group at the alkene terminus, was cyclized to **2d** in 70% yield. The lower yield is due to unidentified side reactions of **1d** under the reaction conditions. Introduction of a diisopropylsilyl group into the substrate at the alkene terminus resulted in a slow cyclization leading to **2e**. Elongation of the reaction time improved the yield of **2e**. Silole **2f**, bearing different substituents (R^1 = Me, R^2 = Ph) at the ring

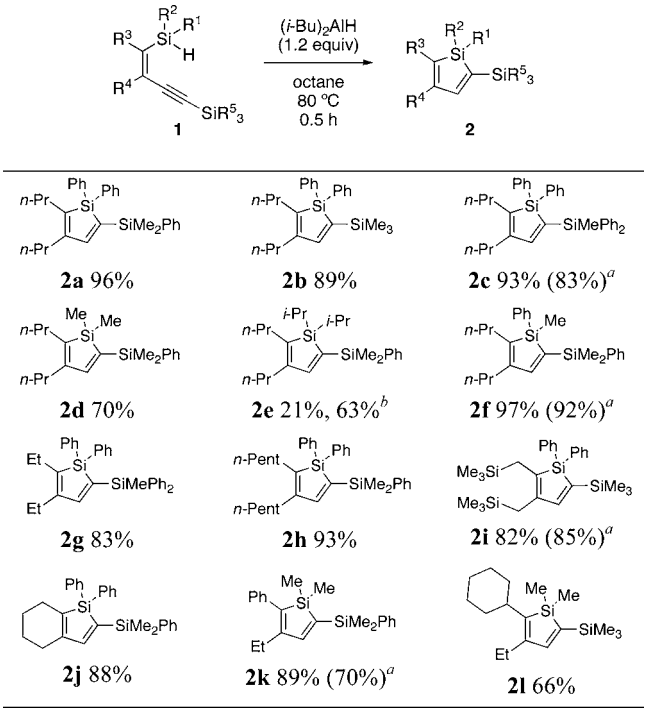
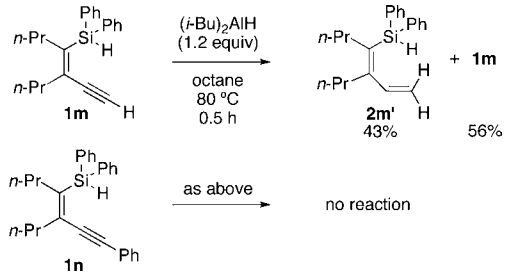


Figure 1. Isolated yields of siloles **2**. Conditions: All reactions were carried out with **1** (0.25 mmol) and DIBAL-H (0.30 mmol) in octane (0.75 mL) at 80 °C for 0.5 h. (a) A substoichiometic amount of DIBAL-H (0.125 mmol) was used. The reaction time was 1 h. (b) The reaction time was 24 h.

silicon, was obtained in excellent yield. The cyclization to siloles **2g** (R^3 = R^4 = Et), **2h** (R^3 = R^4 = n-C_5H_{11}), **2i** (R^3 = R^4 = CH_2SiMe_3), and **2j** (R^3-R^4 = $(CH_2)_4$) also proceeded in good to excellent yields. Siloles **2k** and **2l**, bearing four different substituents at the four ring atoms, could also be prepared from the corresponding enynes **1k** and **1l**. Even with 0.5 equiv of DIBAL-H, the reactions of the selected substrates **1c**, **1f**, **1i**, and **1k** gave the corresponding siloles **2c**, **2f**, **2i**, and **2k**, respectively, in satisfactory yields.

When enyne **1m**, bearing no substituent at the alkyne terminus, was subjected to the standard reaction conditions, only the reduced product **2m′** was formed in 43% yield together with the recovery of **1m** (Scheme 3). Nonsilylated

Scheme 3. Reactivity of Enynes 1m and 1n



internal alkyne **1n** was inert under the same conditions and was recovered quantitatively. These results indicate that the silyl group at the alkyne terminus (SiR^5_3 in **1**) is crucial for the present transformation.

We next examined the application of the DIBAL-H-promoted cyclization to benzosilole synthesis (Figure 2).

DOI: 10.1021/acs.orglett.7b00038
Org. Lett. 2017, 19, 882−885

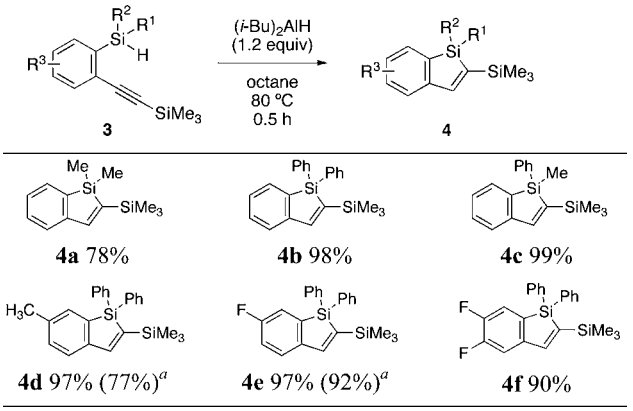
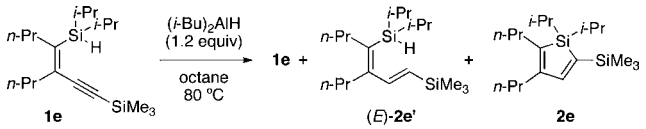


Figure 2. Isolated yields of benzosiloles **4**. Conditions: All reactions were carried out with **3** (0.25 mmol) and DIBAL-H (0.30 mmol) in octane (0.75 mL) at 80 °C for 0.5 h. (a) A substoichiometic amount of DIBAL-H (0.125 mmol) was used. The reaction time was 1 h.

There are several intriguing methods for the synthesis of benzosiloles from hydrosilanes.[6,11−13] However, to the best of our knowledge, use of DIBAL-H for this purpose has been unknown so far. The treatment of 1-hydrosilyl-2-(silylethynyl)-benzenes **3a** with DIBAL-H gave the desired benzosilole **4a** in 78% yield under the standard conditions. The cyclization to other benzosiloles **4b−f** successfully proceeded in excellent yields. Similar to the case of **1**, a substoichiometric amount of DIBAL-H was enough for efficient cyclization of **3d** and **3e**.

As shown above (Figure 1), the cyclization of enyne **1e** required a prolonged reaction time. The reaction for 30 min resulted in 76% conversion of **1e** to give the reduced, uncyclized product (*E*)-**2e′** as the major product as well as the desired product **2e** (Table 2, entry 1). The *Z*-isomer of **2e′**

Table 2. Time Variations of Reaction of Enyne 1e[a]



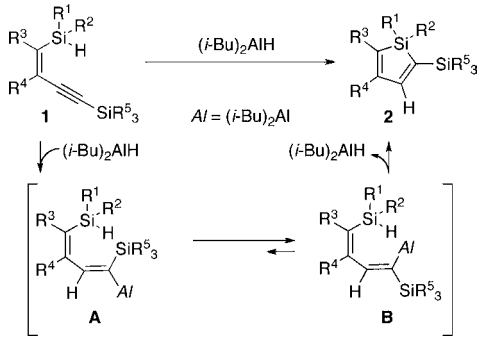
		yield[b] (%)		
entry	time (h)	**1e**	(*E*)-**2e′**	**2e**
1	0.5	24	26	21
2	1	7	11	43
3	24	0	0	63[c]

[a]The reactions were carried out with **1e** (0.25 mmol) and DIBAL-H (0.30 mmol) in octane (0.75 mL) at 80 °C. [b]NMR yield (Bn_2O was used as an internal standard). [c]Isolated yield.

was not detected in the reaction mixture. The conversion at 1 h reached 93% (entry 2). At this reaction time, **2e** became the major product with a decrease in the yield of (*E*)-**2e′**. After 24 h, both **1e** and (*E*)-**2e′** were completely consumed, and only silole **2e** could be identified as a product (entry 3).

The capture of (*E*)-**2e′** and the time variations of the reaction of **1e** suggest that the reaction mechanism involves hydroalumination of the alkynylsilane moiety of **1** with DIBAL-H, geometrical isomerization of the initially formed alkenylalanes **A** to **B**,[9,14] and subsequent intramolecular silicon−carbon bond formation (Scheme 4). Since triorganosilyl groups at the sp-carbon are known to promote alkyne hydroalumination and geometrical isomerization of the resulting alkenylalanes,[9,14] the

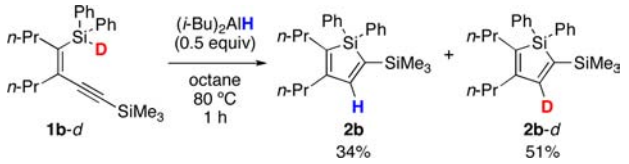
Scheme 4. Plausible Mechanism for Formation of Siloles 2



essential role of the alkynylsilane moiety for the present cyclization (Scheme 3) agrees with the proposed mechanism. Unlike the reaction of **1e**, the formation of alkenylalane (*E*)-**2a′** from **1a** was not detected even at the time when **1a** was not fully converted (Table 1, entry 5). This difference between the reactions of **1a** and **1e** indicates that the silicon−carbon bond-forming step with **1a** is much faster than that with **1e** and that the reaction rate is sensitive to steric congestion around the silicon atom. Therefore, it is likely that the intramolecular reaction of alkenylalanes **B** proceeds by nucleophilic attack of the α-carbon to the silicon center.[15]

The efficient cyclization with a substoichiometric amount of DIBAL-H implied the regeneration of DIBAL-H in the silicon−carbon bond-forming reaction of **B**. To prove this hypothesis, a deuterium-labeling experiment was conducted as shown in Scheme 5. The reaction of deuterated enyne **1b**-*d* with 0.5

Scheme 5. Deuterium-Labeling Experiment

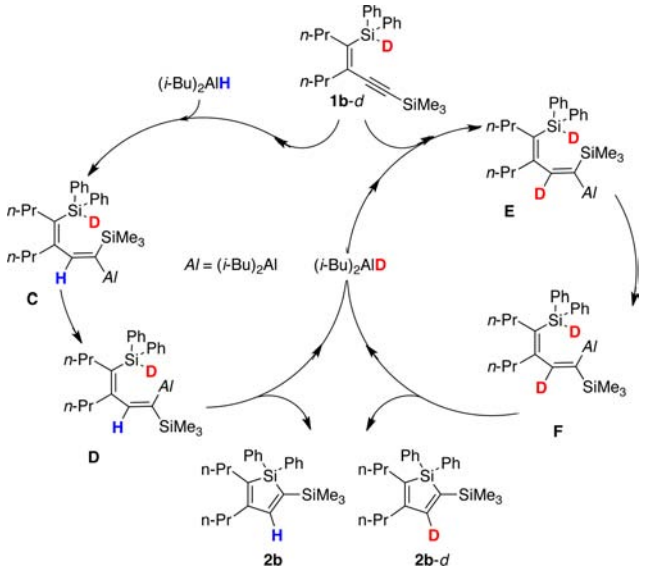


equiv of DIBAL-H at 80 °C for 1 h gave nondeuterated silole **2b** and 3-deuterated silole **2b**-*d* in 34% and 51% yields, respectively. On the basis of the proposed mechanism in Scheme 4, this result can be reasonably explained by the following series of events (Scheme 6). The first reaction sequence promoted by DIBAL-H proceeds via alkenylalanes **C** and **D** to form **2b** and DIBAL-D [$(i\text{-Bu})_2$AlD]. The second or subsequent reaction sequence (cycle) is promoted by the regeneratable DIBAL-D to give **2b**-*d* via alkenylalanes **E** and **F**. From this consideration, the formation of **2b**-*d* is indicative of the generation of DIBAL-D from **D**. Thus, the result of the deuterium-labeling experiment supports the regeneration of DIBAL-H from **B** (Scheme 4). Although the origin of the low catalytic turnover number of DIBAL-H is not clear, the deactivation of DIBAL-H is possibly due to thermal decomposition and the reaction with adventitious air (H_2O and O_2) and the siloles formed.

In summary, we have developed an efficient method for preparing unsymmetrically substituted siloles from 1-hydrosilyl-4-silyl-1,3-enynes and DIBAL-H with complete regioselectivity. This method could be successfully applied to the synthesis of benzosiloles. These reactions successfully proceeded even with a substoichiometric amount of DIBAL-H. The present study has disclosed a novel example of silicon−carbon bond

DOI: 10.1021/acs.orglett.7b00038
Org. Lett. 2017, 19, 882−885

Scheme 6. Plausible Mechanism for Formation of Silole 2b-*d*



formation promoted by DIBAL-H. Derivatization and synthetic application of the siloles and benzosiloles obtained are now under investigation in this laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00038.

Experimental procedures and spectroscopic data for all new compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kmiura@apc.saitama-u.ac.jp.

ORCID

Hidenori Kinoshita: 0000-0002-9761-9015

Katsukiyo Miura: 0000-0002-4535-8677

Notes

The authors declare no competing financial interest.

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DOI: 10.1021/acs.orglett.7b00038
Org. Lett. 2017, 19, 882–885