## An Aza-Brook Rearrangement of (α-Silylallyl)amine

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The Brook rearrangement of  $\alpha$ -silyl alcohol is useful in synthetic organic chemistry.<sup>1</sup> In this reaction, an alkoxy anion attacks the silyl group to produce an  $\alpha$ -alkoxy anion, and a new carbon–carbon bond is formed at the carbon  $\alpha$  to the alkoxy group. In the case of  $\alpha$ -silylallyl alcohol, an allyl anion is formed by Brook rearrangement and the carbon–carbon bond is formed at the  $\alpha$ - or  $\gamma$ -position of the allyl alcohol.<sup>2</sup> However, there are few reports on the Brook-type rearrangement of  $\alpha$ -silylamine.<sup>3</sup> We report here a new carbon–carbon bond formation using an aza-Brook rearrangement (Scheme 1).

We previously reported the synthesis of ( $\alpha$ -silylallyl)amine **3** from alkyne **1** and  $\eta^2$ -iminosilaacyl complex **2**, which was prepared by the insertion of isonitrile **5** into the silyl-zirconium bond of complex **4**, in the presence of LiEt<sub>3</sub>BH<sup>4</sup> in a one-pot reaction. In this reaction,  $\eta^2$ iminosilaacyl complex **2** reacts with LiEt<sub>3</sub>BH to give azazirconacyclopropane **6**, and insertion of alkyne **1** into the zirconium-carbon bond of **6** occurs to give azazirconacyclopentene **7**, which is hydrolyzed to produce ( $\alpha$ silylallyl)amine **3**. Using this procedure, ( $\alpha$ -silylallyl)amines **3a**, **3b**, and **3c** were prepared from the corresponding alkynes **1a**, **1b**, and **1c** in good to moderate yields (Scheme 2).

To a THF solution of ( $\alpha$ -silylallyl)amine **3a** was added BuLi at -78 °C, and the solution was stirred at the same temperature for 30 min. To this solution was added MeI at -78 °C, and the solution was stirred at the same temperature for 30 min. After the usual workup, the methylation product **8a**, the methyl group of which was introduced at the carbon  $\gamma$  to the allylamine, was obtained in 40% yield along with allylsilane **9** in 20% yield.<sup>5</sup> The desired alkylation product **8a** was obtained in a quantitative yield with the addition of HMPA. These results indicate that an aza-Brook rearrangement occurs; i.e., the silyl group of ( $\alpha$ -silylallyl)amine **3a** migrates from carbon to nitrogen and an allyl anion **10** is produced (Scheme 3).

To confirm the generation of the allyl anion by an aza-Brook rearrangement, the deuterated ( $\alpha$ -silylallyl)amine **3a**-d,<sup>4</sup> which was prepared from **1a** and **2** in the presence of LiEt<sub>3</sub>BD, was reacted with BuLi and then treated with alkyl halide **11b** (Scheme 4). After acid hydrolysis, the deuterated aldehyde **12b**-d was obtained in 60% yield (Dcontent > 90 %). This means that the deuterium at the

(4) Honda, T.; Satoh, S.; Mori, M. *Organometallics* **1995**, *14*, 1548. (5) Compound **9** was formed by migration of the silyl group from the nitrogen to the  $\gamma$  carbon of *N*-(silylallyl)anion **10** and subsequent N-methylation.



Scheme 1

allylic position of **3a**-*d* is not abstracted by BuLi, while the nitrogen proton is directly abstracted by BuLi to produce the lithium amide, which attacks the silyl group on the carbon  $\alpha$  to nitrogen to produce *N*-silylallyl anion **10**-*d*.<sup>4</sup> As a result, a carbon–carbon bond is formed at the carbon  $\gamma$  to the allylamine. Moreover, the results indicate that two functional groups are introduced to each alkyne carbon, respectively. One is the formyl group derived from the  $\eta^2$ -iminosilaacyl complex and the other is an electrophile, which is introduced by aza-Brook rearrangement (Figure 1).

( $\alpha$ -Silylallyl)amine **3a** was reacted with various alkyl halides, and the results are shown in the Table. The results indicate that the allyl, benzyl, and alkyl halides can be introduced to the carbon  $\gamma$  to the allylamine **3**.

<sup>(1)</sup> Brook, A. G. Acc. Chem. Res. 1974, 7, 77.

<sup>(2)</sup> Yamamoto, Y. *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, 1991; Vol. 1, p 55.
(3) For the synthesis of (α-silylalkyl)amine: (a) Okazaki, S.; Sato,

<sup>(3)</sup> For the synthesis of ( $\alpha$ -silylalkyl)amine: (a) Okazaki, S.; Sato, Y. *Synthesis* **1990**, 36. (b) Beak, P.; Kerrick, S. T.; Wu, S.; Chu, J. *J. Am. Chem. Soc.* **1994**, *116*, 3231. (c) Sakuragi, A.; Shirai, N.; Sato, Y.; Kurono, Y.; Hatano, K. *J. Org. Chem.* **1994**, *59*, 148. (d) Labreque, D.; Nwe, K. T.; Chan, T. H. *Organometallics* **1994**, *13*, 332. (e) Katritzky, A. R.; Hong, Q.; Yang, Z. *Organometallics* **1995**, *14*, 734. (f) Murai, T.; Oda, T.; Kimura, F.; Onishi, H.; Kanda, T.; Kato, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2143.



## Figure 1.

The alkyl iodide gives slightly better results than the alkyl bromide, in terms of the yield of the desired product **12** (Table 1, runs 1 and 2).

In conclusion, an aza-Brook rearrangement of ( $\alpha$ -silylallyl)amine, which was easily prepared from alkyne and an  $\eta^2$ -iminosilaacyl complex in the presence of LiBEt<sub>3</sub>H, has been realized. Two new carbon–carbon

 
 Table 1. Reaction of 3a-c with E-X Followed by Acid Hydrolysis

run	substrate	E-X 11	product yield (%)
1	<b>3a</b> , $R^1 = R^2 = Pr$	BnO(CH <sub>2</sub> ) <sub>3</sub> -I ( <b>11b</b> )	12b (67)
2	3a	BnO(CH <sub>2</sub> ) <sub>3</sub> -Br ( <b>11b</b> ')	12b (59)
3	<b>3b</b> , $R^1 = Ph$ , $R_2 = {}^{n}C_5H_{11}$	$CH_2 = CHCH_2 - Br$ (11c)	13 (92)
4	<b>3c</b> , $R^1 = {}^nC_5H_{11}$ , $R_2 = H$	BnO(CH <sub>2</sub> ) <sub>3</sub> -I ( <b>11b</b> )	14 (36) <sup>a</sup>
5	3a	$CH_2 = CHCH_2 - Br (11c)$	12c (66)
6	3a	Bn–Br ( <b>11d</b> )	12d (51)
7	3a	Pr-Br ( <b>11e</b> )	12e (59)
8	3a	Ph(CH <sub>2</sub> ) <sub>3</sub> -Br (11f)	<b>12f</b> (57)

<sup>a</sup> The yield of the corresponding alcohol (NaBH<sub>4</sub>/MeOH).

bonds are formed for each alkyne carbon, respectively. Further studies are in progress.

**Supporting Information Available:** Typical procedure and compound characterization data (5 pages).

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