# Regioselective Ring Opening of 1-Methyl-1-(1-naphthyl)-2,3-benzosilacyclobut-2-ene by Carbanion and Silyl Anion

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Ring opening of 1-methyl-1-(1-naphthyl)-2,3-benzosilacyclobut-2-ene by carbanion and silyl anion was found to proceed regioselectively.

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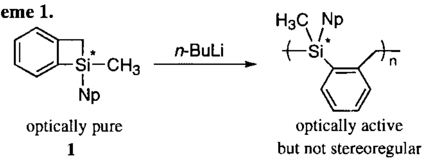
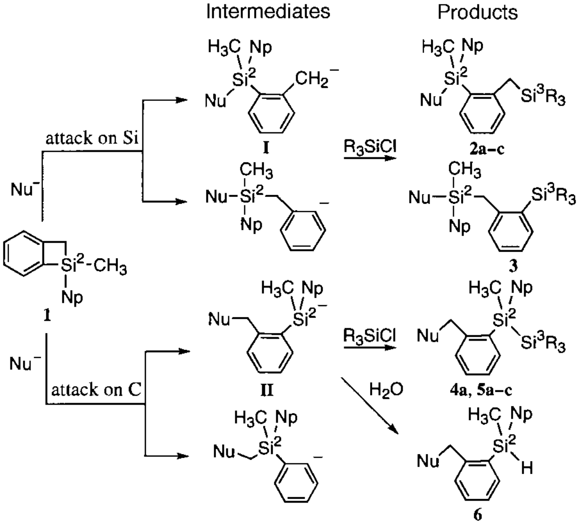
Recently we found that ring opening of an optically pure 1-methyl-1-(1-naphthyl)-2,3-benzosilacyclobut-2-ene **1**[1] by *n*-butyllithium (*n*-BuLi) gave an optically active polymer (Scheme 1).[2] However, the formed polymer did not have well-controlled stereochemical structure of the backbone. To obtain more insights about the regioselectivity of the reaction, the ring opening of **1** by alkyl- and silyllithium was studied.

**Scheme 1.**



When nucleophilic substitution reaction occurs on **1**, two atoms are possibly attacked, namely, Si and methylene carbon. There are two possible modes in ring opening via Si–methylene carbon or Si–aromatic carbon scission to give four intermediates including **I** and **II** as shown in Scheme 2.

**Scheme 2.**



$\mathbf{2}$ : Nu = $n$-Bu, $\mathbf{4}$ : Nu = $Ph_3Si$, $\mathbf{5}$, $\mathbf{6}$ : Nu = $Ph_2(CH_3)Si$.
$R_3 = R^1,R^2,R^3$, **a** : $R^1 = R^2 = R^3 = CH_3$, **b** : $R^1 = R^2 = CH_3$, $R^3$ = Ph,
**c** : $R^1 = CH_3$, $R^2 = R^3$ = Ph.

In the reaction of **1** with *n*-BuLi in the presence of trimethylchlorosilane (TMCS), a product[3] is obtained. In the $^1H$ NMR, benzyl methylene protons adjacent to Si atom appeared as a singlet at δ = 2.10, indicating the attack of *n*-BuLi on the Si atom of **1**. The product is considered either **2** or **3**. The structure of the product was further elucidated by $^{29}Si$ NMR. The $^{29}Si$ chemical shifts of the compounds produced with various nucleophiles and trapping agents, together with those of model compounds are summarized in Tables 1 and 2. $Si^1$, $Si^2$, and $Si^3$ indicate Si atoms originated from the nucleophile, **1**, and the trapping agent, respectively.

**Table 1.** $^{29}Si$ chemical shifts of ring-opened products[a]

| No. | Nucleophile | Trapping agent | Product | Yield / % | δ $Si^1$ | δ $Si^2$ | δ $Si^3$ |
|---|---|---|---|---|---|---|---|
| 1 | *n*-BuLi | $(CH_3)_3SiCl$ | **2a** | 97 | — | −8.11 | 1.56 |
| 2 | | $(CH_3)_2PhSiCl$ | **2b** | 68 | — | −8.07 | −3.74 |
| 3 | | $CH_3Ph_2SiCl$ | **2c** | 98 | — | −8.11 | −8.59 |
| 4 | $Ph_3SiLi$ | $(CH_3)_3SiCl$ | **4a** | 43 | −12.58 | −20.78[b] | −17.34[b] |
| 5 | $CH_3Ph_2SiLi$ | $(CH_3)_3SiCl$ | **5a** | 39 | −8.53 | −20.69[b] | −17.30[b] |
| 6 | | $(CH_3)_2PhSiCl$ | **5b** | 92 | −8.64 | −20.52[b] | −20.25[b] |
| 7 | | $CH_3Ph_2SiCl$ | **5c** | 79 | −8.82 | −20.03[b] | −21.60[b] |
| 8[c] | | $H_2O$ (acidic) | **6** | 34 | −8.33 | −24.13 | — |

[a]The reactions were carried out by adding a nucleophile (5 mol amt.) to the mixture of **1** (1 mol amt.) and the trapping agent (**4** mol amt.) (ref 3). [b]Tentatively assigned. [c]After a nucleophile was added to **1**, the system was stirred for 5 min, and acidic water was added to the reaction mixture (ref 5).

**Table 2.** $^{29}Si$ chemical shifts of $SiR^1R^2R^3R^4$ as model compounds

| Compound | Substituents $R^1$ | $R^2$ | $R^3$ | $R^4$ | δ |
|---|---|---|---|---|---|
| **7** | *n*-Bu | $CH_3$ | $CH_2Ph$ | Np | −2.12 |
| **8** | *n*-Bu | $CH_3$ | Ph | Np | −7.45[a] |
| **9** | $CH_3$ | $CH_3$ | $CH_3$ | Ph | −4.10 |
| **10** | $CH_3$ | $CH_3$ | $CH_3$ | $CH_2Ph$ | 1.30[b] |
| **11** | $CH_3$ | $CH_3$ | Ph | $CH_2Ph$ | −3.77[c] |
| **12** | $CH_3$ | Ph | Ph | $CH_2Ph$ | −8.53[d] |
| **13** | Ph | Ph | Ph | $CH_2Ph$ | −12.21[e] |

Corresponds to [a]$Si^2$ of **2a–c**. [b]$Si^3$ of **2a**. [c]$Si^3$ of **2b**. [d]$Si^3$ of **2c** and $Si^1$ of **5a–c** and **6**. [e]$Si^1$ of **4a**.

Two signals are seen for the product at δ = –8.11 and 1.56. Since nucleophile is *n*-BuLi and trapping agent is TMCS, $Si^2$ and $(CH_3)_3Si^3$ of the compound are considered to appear at around δ = –7.45 and 1.30 for **2** and at around δ = –2.12 and –4.10 for **3** by referring to the chemical shifts of model compounds **7**–**10** in Table 2. The data clearly gave the evidence that the product is 1-{butylmethyl(1-naphthyl)silyl}-2-(trimethylsilylmethyl)benzene, **2a**. Contrary to that the signal at around δ = –8.11 (dialkyldiaryl-substituted $Si^2$) remains almost the same for **2a**–**c**, the other signal ($Si^3$) shifted from δ = 1.56 to –8.59 with increasing number of aromatic groups on $Si^3$, which well agreed with the change for $(CH_3)_3\mathit{Si}CH_2Ph$ : δ = 1.30 (**10**), $(CH_3)_2Ph\mathit{Si}CH_2Ph$: δ = –3.77 (**11**), and $(CH_3)Ph_2\mathit{Si}CH_2Ph$ : δ = –8.53 (**12**). **2c** showed very close two signals at δ = –8.11 and –8.59, which indicates that the two Si atoms ($Si^2$, $Si^3$) are dialkyldiaryl-substituted Si atoms. All these data support that **2a–c** have the same basic structure. The compounds produced with dimethylphenylchlorosilane and methyldiphenylchlorosilane as trapping agent were concluded as 1-{butylmethyl(1-naphthyl)silyl}-2-(dimethylphenylsilylmethyl)benzene **2b** and 1-{butylmethyl(1-naphthyl)silyl}-2-(diphenylmethylsilylmethyl)benzene **2c**. Phenyl- and benzyllithium are also concluded to have attacked on Si atom regioselectively. When triphenylmethyllithium is used, the reaction is very slow, and a ring-opened product was obtained in only 9% yield even after 1h, although the nucleophile had attacked regioselectively on Si atom.

Thus it was concluded that an alkyllithium attacks on Si atom of **1** and that the ring is selectively cleaved at Si–methylene carbon bond to give intermediate **I**, which gives the final products **2a–c** by trapping agent.

When triphenylsilyllithium[4] and methyldiphenylsilyllithium[4] were used as silyllithiums with bulky substituents, only one product was obtained almost exclusively in both cases, although the yield was moderate. These compounds show three $^{29}$Si signals at around $\delta$ = –12.58, –20.78, –17.34 (**4a**) and –8.53, –20.69, –17.30 (**5a**), respectively. To make the assignment of the products easier, the reaction was stopped with water, dimethylphenylchlorosilane and diphenylmethylchlorosilane, and products **6**, **5b** and **5c** were obtained. In the $^1$H NMR of **6**[5], two signals were observed at $\delta$ = 5.34 [Si$^2H$(q)] and 0.61 [Si$^2$(H)C$H_3$(d)]. The signals at $\delta$ = 2.84 and 2.73, appeared as two doublets ($J$ = 14.4 Hz) under the influence of asymmetric Si$^2$ atom, are assigned to benzyl methylene protons adjacent to Si$^1$ atom. The relatively large coupling constant is caused by the presence of many aromatic substituents on Si$^1$ and Si$^2$ atoms. The signal at $\delta$ = –24.13 in $^{29}$Si NMR appeared as a doublet in a coupled spectrum, which indicates that one proton is attached to the Si atom. Accordingly, the signal at $\delta$ = –8.33 can be assigned to Si$^1$ of **6** originated from the nucleophile. Based on these facts, the silyl anion is concluded to have attacked on methylene carbon, and not on Si atom of **1**, to regenerate a silyl anion intermediate **II** which in turn gives 1-{methyl(1-naphthyl)silyl}-2-(diphenylmethylsilylmethyl)benzene **6** when trapped with water.

When a chlorosilane is used as a trapping agent, disilane linkage will be formed from **II**, and **4**, **5** will be obtained. The two signals from $\delta$ = –17 to –21 of **4a**, **5a**, **5b**, and **5c** are reasonably considered to originate from two Si atoms Si$^2$ and Si$^3$ in disilane structure of **4**, **5** by comparing the chemical shifts with model compounds, for example 1,2-dimethyl-1,2,2-triphenyl-1-(1-naphthyl)-disilane ($\delta$ = –21.15, –22.26, model for **5c**). The signals at $\delta$ = –20.78, –20.69, –20.52, –20.03 and –17.34, –17.30, –20.25, –21.60 of **4a**, **5a**, **5b** and **5c** are tentatively assigned to Si$^2$ and Si$^3$ in disilane linkage, respectively, because only the chemical shifts of the latter Si$^3$ shifted to upper field by the changing trapping agent (trimethylsilyl : $\delta$ = –17.3; dimethylphenylsilyl : $\delta$ = –20.25; diphenylmethylsilyl : $\delta$ = –21.60).

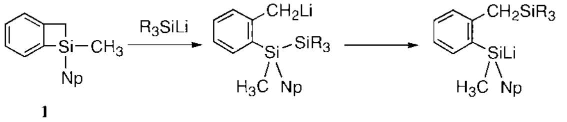
The signals at $\delta$ = –12.58, –8.53, –8.64 and –8.82 of **4a**, **5a**, **5b** and **5c** are reasonably assigned to Si$^1$ of these compounds by comparing with the signals of model compounds **12** and **13** in Table 2. The signals from $\delta$ = –8.5 to –8.8 of **5a**, **5b**, and **5c** are consistent with the presence of CH$_3$*Si$^1$*(Ph)$_2$CH$_2$Ph structure similarly as discussed on Si$^3$ of compound **2c**. The signal at $\delta$ = –12.58 indicates the presence of Ph$_3$*Si*CH$_2$Ph structure in **4a**.

Dimethylphenylsilyllithium[4] gave two compounds after the termination with TMCS, namely, 1-{1,2,2,2-tetramethyl-1-(1-naphthyl)disilyl}-2-dimethylphenylsilylmethylbenzene (75%) as the major product formed by the attack of the nucleophile on methylene carbon of **1** ((CH$_3$)$_2$Ph*Si$^1$*(CH$_2$Ph) : $\delta$ = –3.75), and 1-{1,2,2-trimethyl-1-(1-naphthyl)-2-phenyldisilyl}-2-trimethylsilylmethylbenzene (25%) as the minor product by the attack on Si atom ((CH$_3$)$_3$*Si$^3$*CH$_2$Ph : $\delta$ = 1.45). The regioselectivity of the attack of silyl anion is considered to depend very much on the bulkiness of the substituents on Si atom of the substrate and silyl anion.

Such a regioselectivity in the reaction might be alternatively discussed based on the formation of type **I** intermediate by the initial regioselective attack of silyl anion on Si atom of **1** similarly in the case of carbanion to give **2a,** followed by the internal attack of benzyl anion on the disilane linkage, as shown in Scheme 3. However, the benzyl anion intermediate **I** formed in the ring opening reaction of **1** by *n*-BuLi is highly reactive toward **1**, and the only products could be isolated were oligomers when the reaction was attempted to trap with water. Apparently, the silyl anion intermediate **II** seems less reactive[6] toward **1**, and could be trapped by water to give **6**. It is likely that the silyl anion nucleophile directly attacks on the methylene carbon of **1** to produce intermediate **II**.

In summary, it was found that attack of an alkyllithium and a silyllithium occurs selectively on Si and methylene carbon atom of 1-methyl-1-(1-naphthyl)-2,3-benzosilacyclobut-2-ene, respectively, and that Si–methylene carbon bond of the silacyclobutene ring is selectively cleaved in both cases.

**Scheme 3.**



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Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

**References and Notes**

1 C. Eaborn, D. R. M. Walton, and M. Chan, *J. Organomet. Chem*., **9**, 251 (1967).

2 Details will be published elsewhere.

3 *n*-BuLi (1.59 mol/L, 7.37 mmol) in hexane was added to a solution of **1** (0.383 g, 1.47 mmol) in THF (10 mL) in the presence of TMCS (0.639 g, 5.89 mmol) at –78 °C. After stirred for 1 h, the volatile fractions were removed. The residue was purified by silica-gel column chromatography using hexane as an eluent to give **2a** in 97% (0.556 g, 1.43 mmol) as a colorless liquid. **2a**: $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.89–7.79 (m, 3H), 7.62 (m, 1H), 7.51–7.46 (m, 1H), 7.41–7.36 (m, 1H), 7.30–7.20 (m, 3H), 7.14–7.10 (m, 1H), 7.01–6.98 (m, 1H), 2.10(s, 2H), 1.32–1.24 (m, 6H, CH$_3$(C$H_2$)$_3$), 0.83 (t, 3H, $J$ = 7.2 Hz, C$H_3$CH$_2$), 0.69 (s, 3H), –0.40(s, 9H); FT-MS(EI): *m/z* 390.219 (calcd.: 390.219).

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5 Methyldiphenylsilyllithium (1.65 mol/L, 8.25 mmol) in THF was added to a solution of **1** (0.114 g, 0.440 mmol) in THF (4 mL) at –78 °C. After stirred for 5 minutes, 1 M HCl$_{(aq)}$ was added. **6** was obtained in 34% (0.0687 g, 0.150 mmol) as a colorless liquid by column chromatography (hexane). **6**: $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.96–7.94 (m, 1H), 7.89–7.84 (m, 2H), 7.62–7.60 (m, 1H), 7.47–7.25 (m, 14H), 7.18–7.13 (m, 1H), 7.09–7.07 (m, 1H), 6.86–6.83 (m, 1H), 5.40 (q, 1H, $J$ = 3.9 Hz, Si–$H$), 2.84, 2.73 (two d, 2H, $J_{geminal}$ = 14.4 Hz, Si–C$H_2$Ph), 0.61(d, 3H, $J$ = 3.9 Hz, Si(C$H_3$)H), 0.35(s, 3H, CH$_2$Si(Ph)$_2$(C$H_3$)); FT-MS(EI): *m/z* 458.187 (calcd: 458.188).

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