## SYNTHESIS OF 4-SUBSTITUTED 1,1-DI-t-BUTYLBENZOSILACYCLOBUTENES

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Bromination of l,l-di-t-butyl-2,3-benzo-l-silacyclo-2-butene with N-bromosuccinimide gave its 4-bromo derivative. Metallation with <u>n</u>-Bu<sub>2</sub>CuLi followed by alkylation or acylation gave the corresponding 4-alkyl or acyl derivatives. Replacement of the bromine atom with alkoxyl group was achieved by treatment with alcohol in the presence of  $AgBF_4$ .

There has been considerable interest in the chemistry of small ring silicon compounds.<sup>1)</sup> However, reports on silacyclobutenes are relatively rare.<sup>2)</sup> This may be due to the lack of general synthetic routes to silacyclobutenes.<sup>3)</sup> Besides, silacyclobutenes are known to undergo facile ring opening with Si-C bond rupture as a result of nucleophilic attack at silicon.<sup>3a,b)</sup> Therefore, it has been difficult to introduce substituents in silacyclobutenes.

We now wish to report the synthesis of 1, 1-di-t-buty1-2, 3-benzo-1-silacyclo-2-butene (<u>4e</u>) Which is resistant to the nucleophilic attack at the silicon atom. It undergoes ring opening neither in refluxing methanol nor with sodium methoxide at room temperature. This stability of <u>4e</u> towards nucleophiles has made substitution reactions possible.

The reaction of tetrachlorosilane with the Grignard reagent from o-bromobenzyl bromide (<u>1</u>) gave <u>2</u>, which was cyclized to 1,1-dichloro-2,3-benzo-1-silacyclo-2-butene (<u>3</u>) by excess magnesium. The overall yield of <u>3</u> from <u>1</u> was 36%. 1,1-Dialkyl or 1,1-diphenyl-2,3-benzo-1-silacyclo-2-butenes (<u>4a-e</u>)<sup>4</sup>) were prepared from <u>3</u> with either Grignard reagents or <u>t</u>-butyllithium.

 $\alpha$ -Metallation<sup>5)</sup> of <u>4e</u> was achieved by proton abstraction with <u>t</u>-butyllithium in THF-pentane-HMPA-TMEDA at -78°C. The resulting 4-lithio derivative was quenched with methyl iodide to obtain the 4-methyl derivative  $(\underline{6a})$  only in low yield (11%).

A promising approach for functionalization of silacyclobutenes is the introduction of 4-halogen atom which might be exchanged with alkyl, alkoxyl, and acyl groups either via metallation or silver ion-assisted nucleophilic substitution.



i) Mg/ether ii) SiCl<sub>4</sub> iii) excess Mg
iv) RMgX or t-BuLi v) NBS/CCl<sub>4</sub>

4-Bromo-1,1-di-<u>t</u>-buty1-2,3-benzo-1-silacyclo-2-butene  $(\underline{5e})^{4}$  was prepared by reaction of <u>4e</u> and 0.8 equiv. of N-bromosuccinimide (NBS) in refluxing carbon tetrachloride in 30% yield. In the NMR spectrum of <u>5e</u>, the <u>t</u>-butyl groups appear as a pair of singlet at  $\delta$ 1.09 and 1.18 ppm. Formation of <u>5a</u> and <u>5b</u> from <u>4a</u> and <u>4b</u> was confirmed by the NMR spectra of the crude reaction mixtures. However, chromatographic purification of <u>5a</u> and <u>5b</u> was unsuccessful, because of their fast decomposition on silica gel or alumina.

When <u>5e</u> was treated with 4 molar equiv. of lithium dibutylcuprate<sup>6</sup>) in THF at -48 °C, followed by quenching with excess methyl iodide or allyl bromide, 4-alkylbenzosilacyclobutenes, <u>6a</u> and <u>6b</u>, were obtained,<sup>4</sup>) respectively. Treatment with acetyl and benzoyl chloride afforded acyl derivatives, <u>6c</u> and <u>6d</u>,<sup>4</sup>) respectively.

Halogen-copper exchange with lithium dibutylcuprate has been shown to be useful for the alkylation of bromocyclopropanes.<sup>7)</sup>

Bromine-lithium exchange of <u>5e</u> with <u>t</u>-butyllithium followed by treatment with excess methyl iodide failed to give <u>6a</u>. Instead, a reduction product, <u>4e</u> was obtained in 50% yield along with 20% yield of dimeric product 7.<sup>8</sup>



a, R=CH<sub>3</sub>, 65%
b, R=CH<sub>2</sub>CH=CH<sub>2</sub>, 55%
c, R=COCH<sub>3</sub>, 25%
d, R=COPh, 57%

When <u>5e</u> reacted with aqueous acetone in the presence of silver tetrafluoroborate, the cyclic siloxane  $(\underline{9})^{4}$  was isolated (57%). This most likely resulted from the rearrangement<sup>9</sup>) of initially formed  $\alpha$ -silyl carbinol ( $\underline{8}$ ). Treatment with methanol in the presence of AgBF<sub>4</sub>, easily converted <u>5e</u> to the methoxy derivative ( $\underline{10}$ )<sup>4</sup>) in 53% yield.

We thank Professors N. Inamoto and R. Okazaki of the University of Tokyo, Japan, for friendly advice, and Mr. N. Tokitoh for high resolution mass spectra. We thank the Korea Science and Engineering Foundation for financial support.



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5e + CH<sub>3</sub>OH  $\xrightarrow{\text{AgBF}_4}$   $\xrightarrow{\text{OCH}_3}$ si + + + 10 619

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(Received March 7, 1985)