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

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Bromination of 1,1-di-t-butyl-2,3-benzo-1-silacyclo-2-butene with N-bromosuccinimide gave its 4-bromo derivative. Metallation with *n*-Bu_2CuLi 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 $AgBF_4$.

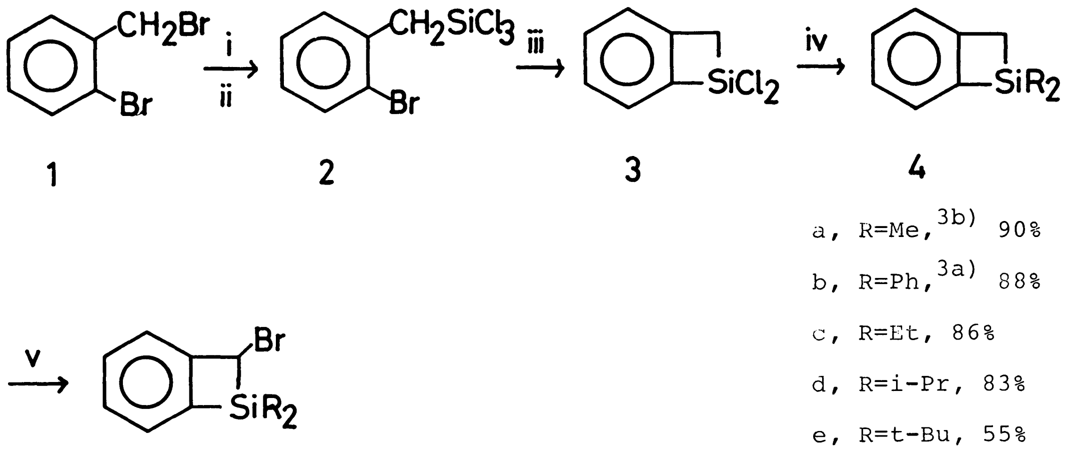
There has been considerable interest in the chemistry of small ring silicon compounds.1) However, reports on silacyclobutenes are relatively rare.2) This may be due to the lack of general synthetic routes to silacyclobutenes.3) Besides, silacyclobutenes are known to undergo facile ring opening with Si-C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

We now wish to report the synthesis of 1,1-di-*t*-butyl-2,3-benzo-1-silacyclo-2-butene (4e) 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 4e towards nucleophiles has made substitution reactions possible.

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

α-Metallation5) of 4e was achieved by proton abstraction with *t*-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 (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.



1 2 3 4

a, R=Me,[3b] 90%
b, R=Ph,[3a] 88%
c, R=Et, 86%
d, R=i-Pr, 83%
e, R=t-Bu, 55%

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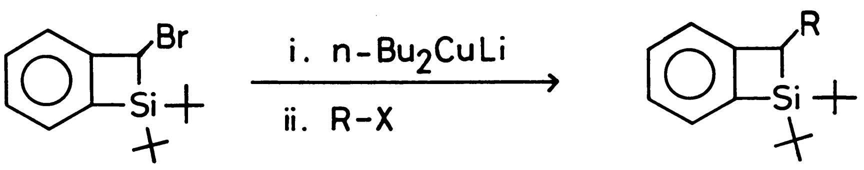
i) Mg/ether ii) $SiCl_4$ iii) excess Mg
iv) RMgX or t-BuLi v) NBS/CCl_4

4-Bromo-1,1-di-t-butyl-2,3-benzo-1-silacyclo-2-butene (5e)[4] was prepared by reaction of 4e and 0.8 equiv. of N-bromosuccinimide (NBS) in refluxing carbon tetrachloride in 30% yield. In the NMR spectrum of 5e, the t-butyl groups appear as a pair of singlet at δ1.09 and 1.18 ppm. Formation of 5a and 5b from 4a and 4b was confirmed by the NMR spectra of the crude reaction mixtures. However, chromatographic purification of 5a and 5b was unsuccessful, because of their fast decomposition on silica gel or alumina.

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

Halogen-copper exchange with lithium dibutylcuprate has been shown to be useful for the alkylation of bromocyclopropanes.[7]

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



5e 6

a, R=CH_3, 65%

b, R=$CH_2CH=CH_2$, 55%

c, R=$COCH_3$, 25%

d, R=COPh, 57%

When 5e reacted with aqueous acetone in the presence of silver tetrafluoroborate, the cyclic siloxane (9)$^{4)}$ was isolated (57%). This most likely resulted from the rearrangement$^{9)}$ of initially formed α-silyl carbinol (8). Treatment with methanol in the presence of $AgBF_4$, easily converted 5e to the methoxy derivative (10)$^{4)}$ in 53% yield.

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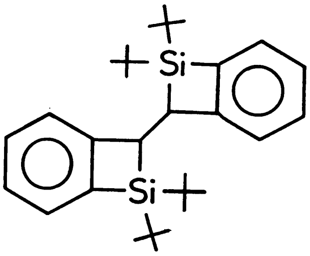

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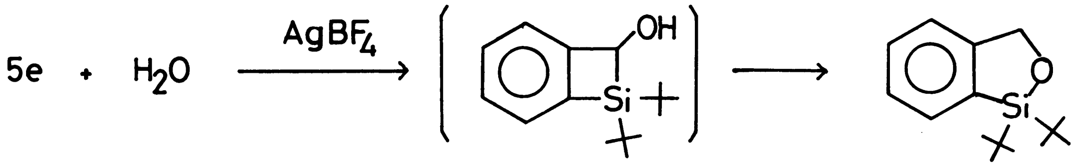

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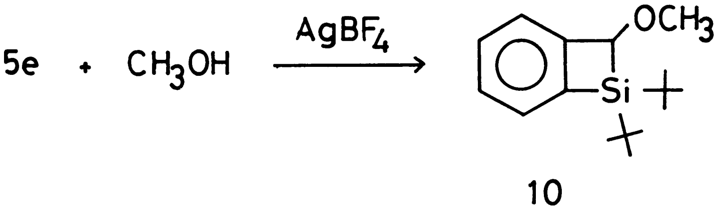

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4) All products gave satisfactory spectral data (IR, ^{1}H-NMR, and high resolution MS). ^{1}H-NMR spectra were recorded at 60 MHz in CCl_4 solution.
4c: ^{1}H-NMR δ0.8-1.3 (10H, m), 2.05 (2H, s), 6.9-7.3 (4H, m).
4d: ^{1}H-NMR δ0.9-1.4 (14H, m), 2.05 (2H, s), 7.0-7.3 (4H, m).
4e: ^{1}H-NMR δ1.01 (18H, s), 2.05 (2H, s), 6.9-7.2 (4H, m).
5e: ^{1}H-NMR δ1.09 (9H, s), 1.18 (9H, s), 4.55 (1H, s), 7.0-7.4 (4H, m).
6a: ^{1}H-NMR δ1.04 (9H, s), 1.06 (9H, s), 1.46 (3H, d, J=7.8 Hz), 2.65 (1H, q, J=7.8 Hz), 6.8-7.3 (4H, m).
6b: ^{1}H-NMR δ1.08 (9H, s), 1.09 (9H, s), 2.48-2.88 (3H, m), 4.77-5.22 (2H, m), 5.50-6.21 (1H, m), 6.9-7.3 (4H, m).
6c: IR (neat) 1750 cm^{-1}; ^{1}H-NMR δ1.02 (18H, s), 1.92 (3H, s), 5.21 (1H, s), 6.8-7.4 (4H, m).
6d: IR (neat) 1730 cm^{-1}; ^{1}H-NMR δ1.09 (18H, s), 6.13 (1H, s), 6.8-7.8 (9H,m).
9: ^{1}H-NMR δ1.00 (18H, s), 4.98 (2H, s), 6.9-7.7 (4H, m).
10: ^{1}H-NMR δ1.05 (9H, s), 1.07 (9H, s), 3.44 (3H, s), 4.40 (1H, s), 6.9-7.5 (4H, m).

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8) The dimer 7 was separated to a pair of diastereomers and a meso compound by preparative TLC (silica gel, hexane). The ^{1}H-NMR spectrum of one is δ1.13 (18H, s), 1.15 (18H, s), 3.23 (2H, s), 7.0-7.4 (8H, m), and the other is δ1.07 (18H, s), 1.21 (18H, s), 3.37 (2H, s), 6.5-7.4 (8H, m). Experiments to determine which is the meso and which is the d,l are in progress.

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