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Cleavage of C–Si bond by intramolecular nucleophilic attack: lithiation-promoted formation of siloles from 1-bromo-4-trisubstituted silyl-1,3-butadiene derivatives

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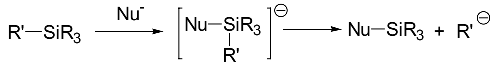
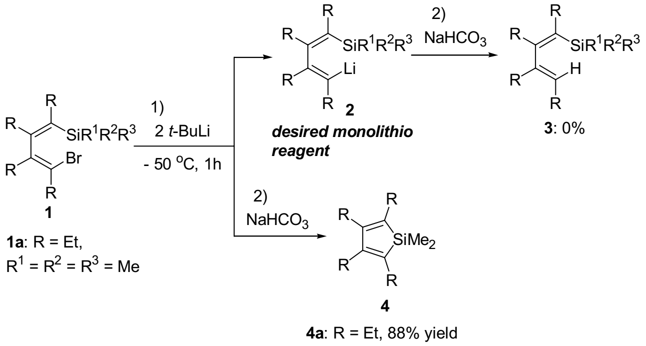
Abstract—Lithiation of 1-bromo-4-trisubstituted silyl-1,3-butadiene derivatives with *t*-BuLi afforded substituted siloles in high yields. Cleavage of one of the three C–Si bonds took place via intramolecular nucleophilic substitution. Selective cleavage was observed when the silyl group possessed different substituents. Results showed that vinyl and phenyl substituents on Si were substituted much more easily than methyl groups, whilst a methyl group was exclusively deleted from an *i*-Pr–SiMe$_2$ moiety.

Nucleophilic activation and substitution of organosilicon groups are fundamental in organosilicon chemistry and in developing synthetic methods.[1] Pentavalent organosilicates have been proposed as key intermediates in organolithium mediated nucleophilic activation and substitution reactions of organosilicon compounds (Eq. 1).[1–6]



$$R'\text{–}SiR_3 \xrightarrow{Nu^-} \left[\begin{array}{c}Nu\text{–}SiR_3\\ |\\ R'\end{array}\right]^{\ominus} \longrightarrow Nu\text{–}SiR_3 + R'^{\ominus} \qquad (1)$$

Our group has been recently interested in reaction chemistry of 1-lithio-1,3-butadiene derivatives.[7–11] These monolithio reagents used in this laboratory are usually generated in situ from their corresponding monohalo compounds and *t*-BuLi. However, when 1-bromo-4-trimethylsilyl-1,3-butadiene **1a** (R = Et, $R^1 = R^2 = R^3 = Me$) was treated with 2 equiv of *t*-BuLi as usually done, no formation of the desired monolithio reagent **2** was observed (Scheme 1). Instead, interestingly, silole derivative **4a** (R = Et) was obtained in 88% yield (Scheme 1). In this paper, we would like to report an alternative procedure for the preparation of silole derivatives and preliminary results on organolithium-promoted substituent-dependent selective cleavage of C–Si bonds.



Scheme 1. Lithiation-promoted formation of siloles from 1-bromo-4-trisubstituted silyl-1,3-butadiene derivatives.

Multi-substituted silacyclopentadienes (siloles) are useful compounds for the study of Si-containing materials.[12] Thus, preparative methods for these compounds have been of interest. Several papers have appeared reporting the synthesis of siloles from typical reactions of dihalosilanes with 1,4-dilithio-1,3-dienes.[12] The reaction reported here (Scheme 1) represents a new method

Keywords: Nucleophilic substitution; Organosilicon compounds; Siloles; Pentaorganosilicates.

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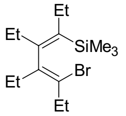
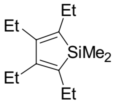
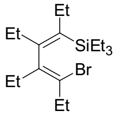
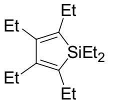
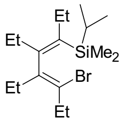
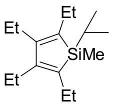
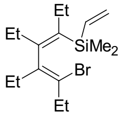
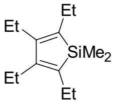
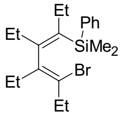
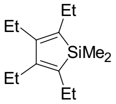
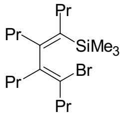
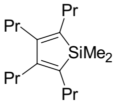
Table 1. Formation of siloles by lithiation of 1-bromo-4-trisubstituted silyl-1,3-butadiene derivatives[a]

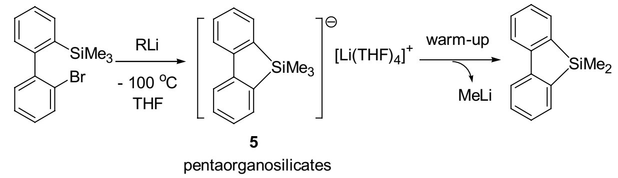
Bromo compound **1**	Product **4**	Yield of **4**/%[b]
 **1a**	 **4a**	88 (60)
 **1b**	 **4b**	(82)
 **1c**	 **4c**	99 (80)
 **1d**	 **4a**	69
 **1e**	 **4a**	78
 **1f**	 **4d**	65 (48)

[a] Reaction conditions are given in Scheme 1.

[b] GC yields. Isolated yields are given in parentheses.

for the preparation of multi-substituted siloles via lithiation-promoted nucleophilic substitution of organosilicon compounds. Representative results are given in Table 1. A variety of substituents on the Si atom, such as methyl, ethyl, isopropyl, vinyl, and phenyl could be used to afford silole derivatives in good to excellent yields.

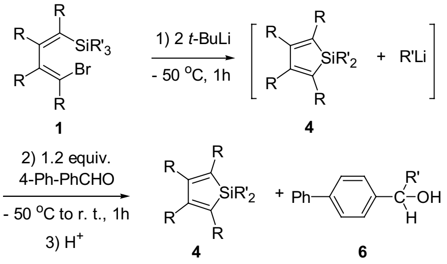
In the case of **1c**, silole **4c** with a methyl group and an isopropyl group was obtained in excellent yield.[13] Obviously, one of the two methyl groups in **1c** was substituted, leaving the bigger isopropyl group untouched. However, in cases of **1d** and **1e**, although other siloles were detected by GC–MS, **4a** was formed as the major product, indicating that the vinyl group in **1d** and the phenyl group in **1e** were much more readily substituted than methyl groups. Kumada and co-workers have studied substitution reaction of siloles.[3] They found that methyl groups on Si atoms of siloles could be replaced by butyl groups in the presence of an excess of BuLi.[3] Pentaorganosilicates were proposed as the intermediates for such substitution reaction. Klumpp and co-workers reported first observation of pentaorganosilicates **5** by low-temperature NMR spectroscopy in a special case (Scheme 2).[6]



Scheme 2.

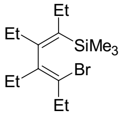
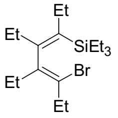
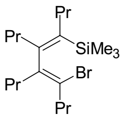
Since a new organolithium species has been proposed to be generated in such substitution reaction, we tried to trap the organolithium species to understand the reaction mechanism for our reaction. The experimental procedure is given in Scheme 3. Table 2 demonstrates results obtained in cases of $SiMe_3$ and $SiEt_3$, in which MeLi and EtLi are proposed to be generated in situ, respectively.

In cases of **1c**,**d**, and **1e** which possess different substituents on the Si atom, trap of organolithium compounds generated in situ following the procedure shown in Scheme 3 with aldehydes was also carried out (Fig. 1). In case of **1c**, only **6a** was isolated in 75% yield, which was consistent with the observation of formation of **4c** (Table 1) as the only silole product. In cases of **1d** and **1e**, a mixture of two alcohols were isolated, respectively. Alcohols **6d** and **6e** with vinyl group or phenyl group were obtained as the major products, while **6a** was obtained in both cases as the minor products (Fig. 1).



Scheme 3. Trapping of organolithium compounds generated in situ.

Table 2. Trapping of MeLi and EtLi with aldehydes[a]

Bromo compound **1**	Yield of **4**/%[b]	Yield of **6**/%[b]
 **1a**	**4a**: (60)	**6a**: R′ = Me (64)
 **1b**	**4b**: (82)	**6b**: R′ = Et (83)
 **1f**	**4d**: (48)	**6a**: R′ = Me (71)

[a] Reaction conditions are given in Scheme 3.

[b] Isolated yields.

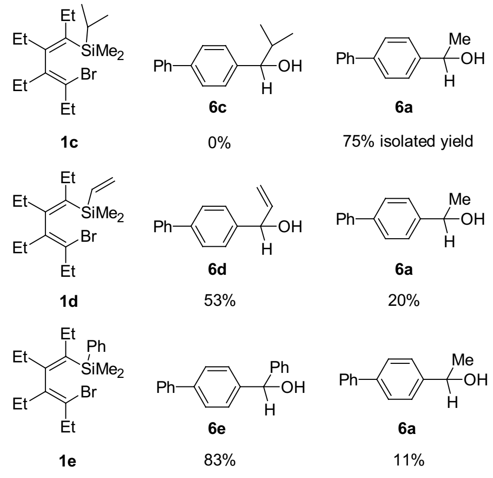
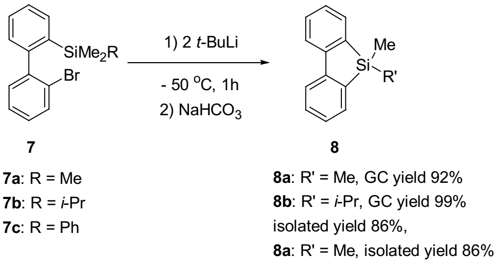


Figure 1.



Scheme 4.

To compare with the system reported by Klumpp and co-workers,[6] we prepared bromides **7** with methyl, isopropyl, and phenyl groups, respectively on the Si atom, and investigated their selectivity of cleavage of Si–C bonds following our procedure (Scheme 4). Results obtained for this system were consistent with those shown in Table 1.

In summary, we have developed a new method for preparation of multi-substituted siloles. A pentaorganosilicate is proposed to be the intermediate for this reaction. Preliminary results show that lithiation-promoted nucleophilic substitution reactions of organosilicon compounds are substituent dependent. This observation is expected to have useful applications for organic synthesis. Further investigation into the reaction mechanism and applications are in progress.

Acknowledgements

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13. A typical experimental procedure for the formation of **4c**. To a solution of **1c** (1.0 mmol) in Et_2O (5 mL) was added *t*-BuLi (1.5 M pentane solution, 2.0 mmol) at −50 °C and the mixture was stirred for 1 h at the same temperature. The reaction mixture was quenched with aqueous $NaHCO_3$ and extracted with diethyl ether. The extract was washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by chromatography on silica gel to afford **4c** as colorless liquid, isolated yield 80% (200 mg), GC yield 99%. NMR data for **4c**: ^1H NMR ($CDCl_3$, $SiMe_4$): δ 0.19 (s, 3H), 0.94–1.05 (m, 18H), 2.12–2.41 (m, 9H). ^{13}C NMR ($CDCl_3$, $SiMe_4$): δ −6.01, 12.90, 14.85, 15.30, 17.67, 20.64, 22.56, 136.42, 154.54. HRMS calcd for $C_{16}H_{30}Si$ 250.2117. Found 250.2121.