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COMMUNICATIONS

Lithio Siloles: Facile Synthesis and Applications

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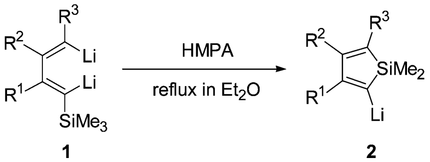
Functionalized siloles have become ever more attractive in recent years, since these types of compounds have practical applications including new π-system organic materials of electronic and optoelectronic devices.[1−3] Among synthetic methods for siloles, the Tamao−Yamaguchi method for in situ generation of 2,5-dilithio siloles and lithio benzosiloles has been demonstrated to be particularly important, because a wide variety of functionalized siloles can be readily synthesized by further applications of 2,5-dilithio siloles and lithio benzosiloles.[1,2] In this Communication, we would like to report a facile synthesis of a new type of lithio siloles **2** from readily available silyl 1,4-dilithio 1,3-butadiene derivative **1**,[4,5] via novel reaction mechanisms (eq 1). These lithio siloles **2** are more general in terms of substitution patterns and synthetic methods, affording diversified structures, as demonstrated by their further applications.



(1)

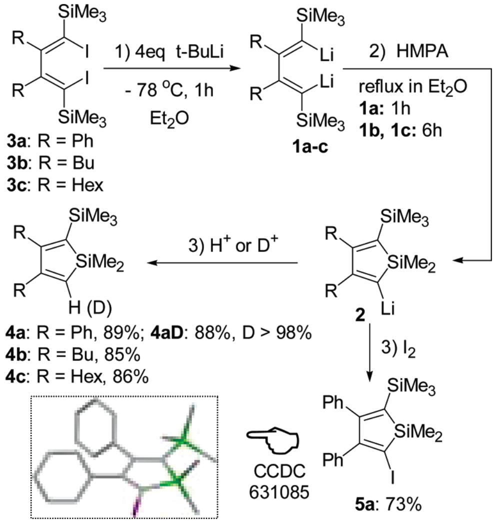
1,4-Bis(trimethylsilyl)-2,3-diphenyl-1,4-dilithio-1,3-diene **1a** (1 mmol) in 5 mL of diethyl ether was quantitatively generated in situ from its corresponding 1,4-diiodo compound **3a** (1 mmol) and *t*-BuLi (4 mmol) at −78 °C (Scheme 1).[4,5] The solution was then heated to reflux in the presence of HMPA and maintained for 1 h. The reaction was very clean, affording the α-silylated silole derivative **4a** in 89% isolated yield upon hydrolysis with water. When the reaction mixture was quenched with D_2O instead, the deuterated compound **4aD** was obtained in 88% isolated yield with D incorporation more than 98%. Similarly, the dibutyl substituted **1b** and the dihexyl **1c** also afforded siloles **4b** and **4c** in 85% and 86% isolated yields, respectively. Termination of the reaction with I_2 afforded 2-iodo-5-trimethylsilyl silole **5a** in 73% isolated yield. The structure of **5a** has been determined by single-crystal X-ray structural analysis (CCDC 631085).

Other types of silylated butadienes were found to undergo similar reactions affording their corresponding siloles (Figure 1). Interestingly, the monosilylated butadiene **1e** and **1f** could also proceed this reaction highly selectively to form silole **4e** and **4f** in 82% and 55% isolated yields, respectively.

All the above results indicated that 1,4-dilithio-1,3-dienes **1** underwent novel intramolecular skeletal rearrangements affording the very useful lithio silole derivatives **2**.

As demonstrated in Figure 2, these readily and efficiently generated lithiosiloles **2** can be applied for the synthesis of a variety of functionalized siloles in one-pot. Diversified utilization of the unique structures of thus obtained siloles can be further expected.

Scheme 1



The reaction mechanism is very intriguing. Given in Scheme 2 are two proposed mechanisms for this useful reaction. First, the electrocyclic ring-closing of **1** giving **6** is assumed to be a key step for path a.[6] It has been well-documented that (1*Z*,3*Z*)-1,4-dilithio-1,3-butadienes like **1** generally take the s-cis conformation and a double-bridged dilithium structure,[7,8] which is proposed to be the crucial factor leading to the unprecedented facile electrocyclic formation of **6**.[6] For path b, the reversion of the stereochemistry at the terminal carbon bonding with a Li atom and a $SiMe_3$ group of **1** forming **8** is assumed to be the essential step. Configurational E/Z isomerization of 1-(trimethylsilyl)-1-alkenyllithium compounds has been reported in the literature.[9,10] Then, an intramolecular anionic attack on the adjacent $SiMe_3$ group followed by release of MeLi might result in the formation of 2-lithiosiloles **2**.[11] When the reaction was carried out without HMPA, no formation of **2** was

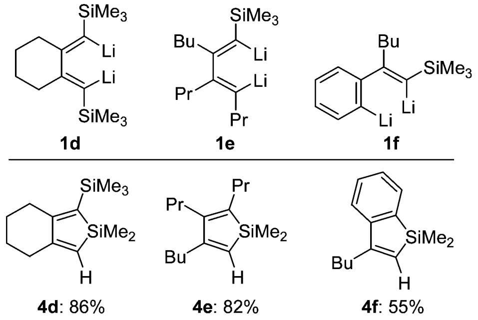


Figure 1.

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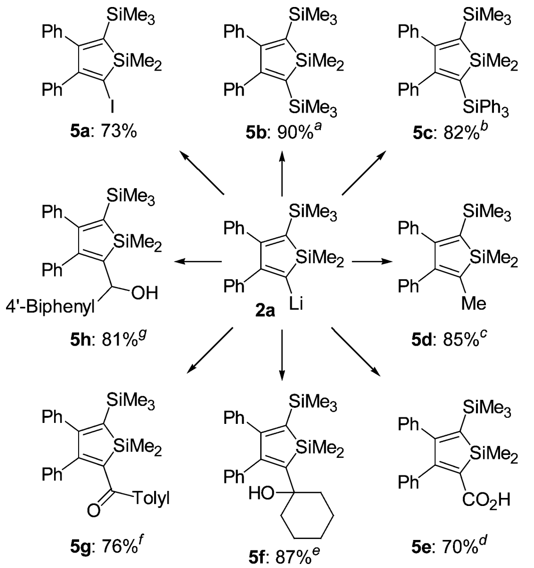
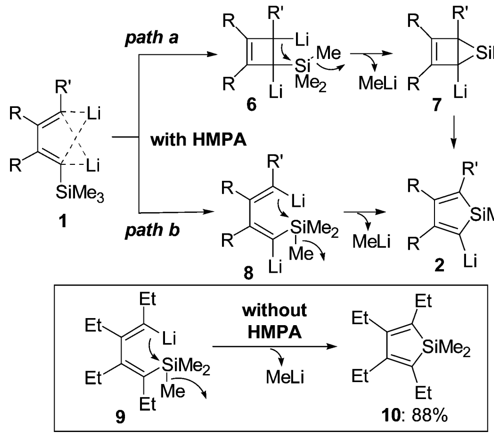


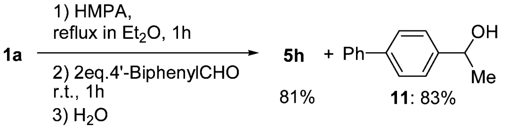
Figure 2. One-pot synthesis of **5** via **2a** and (a) $SiMe_3Cl$; (b) $SiPh_3Cl$; (c) MeI; (d) CO_2; (e) cyclohexanone; (f) 4′-tolylCOCl; (g) 4′-biphenylCHO.

Scheme 2



observed, which is in sharp contrast to some previous results.[11] For example, without HMPA, the intramolecular anionic attack of **9** gave **10** in 88% yield.[11a] In addition, no formation of **8** or related isomers was detected under various experimental conditions in this work.[9,10] Thus, although path b seems more likely, the mechanism via path a cannot be ruled out.

Indeed, the in situ generated MeLi was trapped by an aldehyde forming the alcohol **11** in 83% isolated yield (eq 2).[11a]



(2)

In conclusion, we report in this paper a new type of lithio siloles, which can be complementary to those Tamao−Yamaguchi reagents.[1,2] These new lithio siloles have the following features: (1) readily available; (2) more general in terms of substitution patterns and structural diversity; (3) formed via novel reaction patterns. Further investigation into the reaction mechanism, scope, and applications is in progress.

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Supporting Information Available: Experimental details, copies of ^1H and ^{13}C NMR spectra for all isolated compounds and crystallographic data for **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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