Tetrahedron Letters, Vol.32, No.18, pp 2049-2052, 1991
Printed in Great Britain

0040-4039/91 $3.00 + .00
Pergamon Press plc

Unusual 1,3-Rearrangement of Trimethylsilyl Group in the Reaction of 2,4,6-Tris[bis(trimethylsilyl)methyl]phenyllithium

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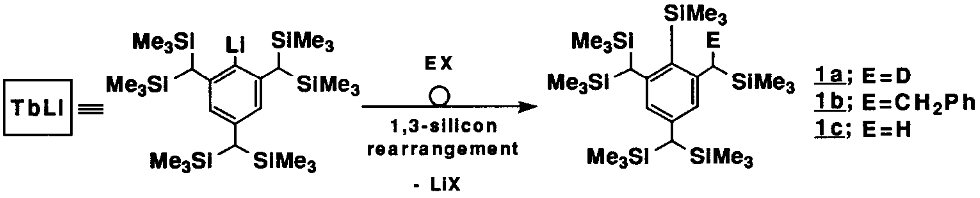
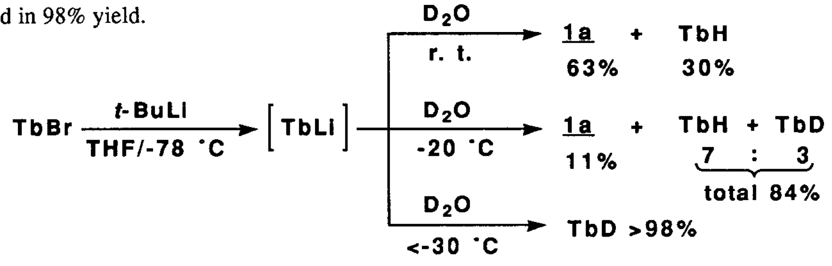
Summary; 2,4,6-Tris[bis(trimethylsilyl)methyl]phenyllithium (**TbLi**) gave a novel 1,3-silicon rearrangement product above -30 °C, while the treatment of **TbLi** with some electrophiles also afforded 1,3-silicon rearrangement products even at -78 °C probably *via* single electron transfer mechanism.

Rearrangement reactions with migration of silicon atom have attracted much attention from a standpoint of not only the mechanistic interest but also their potential synthetic utility.[1] Among them are a variety of 1,3-migration reactions of a silyl group from heteroatom to carbon (or *vice versa*) or heteroatom to heteroatom.[2] However, there has been no established example of 1,3-silyl group shift from carbon to carbon except for the thermal 1,3-sigmatropic rearrangement of allylsilanes in the high temperature (500 °C) gas phase reactions[3] and the photochemical 1,3-silicon migration of benzylsilanes[4a] and allylsilanes.[4b]

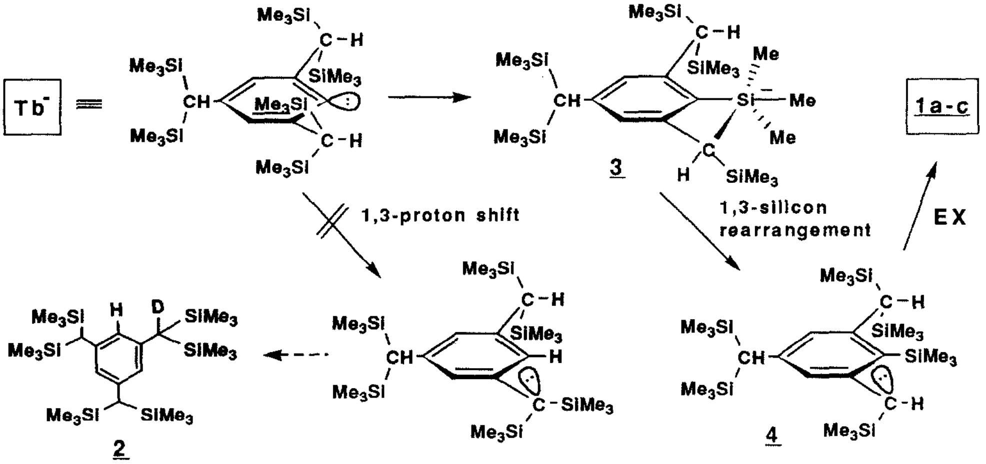
We have recently reported that 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as **Tb** hereafter in this paper) is a usuful protective group for kinetic stabilization of highly reactive species such as *N*-thiosulfinylaniline (**Tb-N=S=S**),[5] and also estimated the bulkiness of this new sterically demanding group by the enolate formation reaction using **TbLi** as a base.[6] Here we have investigated the thermal stability and some reactivity of **TbLi** and found an unusual 1,3-silicon rearrangement in this unique polysilylated bulky aryllithium.



When a light yellow THF solution of **TbLi** generated by lithiation of **TbBr** with 2.2 eq. of *t*-BuLi (1.6 *N* in pentane) at -78 °C was treated with an excess amount of deuterium oxide (D_2O) at this temperature, only **TbD** was isolated in 98% yield.

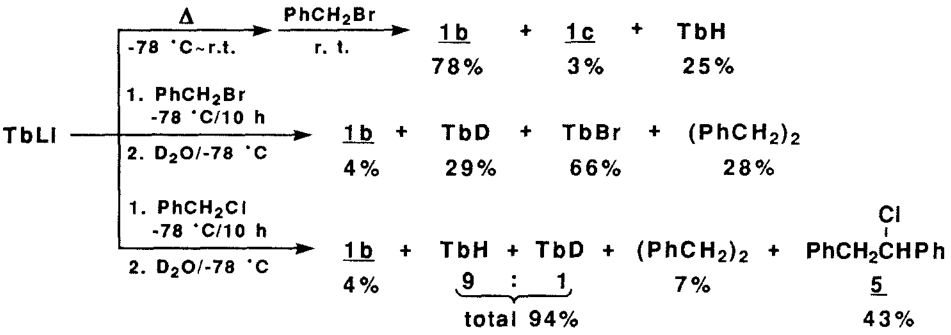


D_2O addition to the **TbLi** solution at -30 °C also resulted in a quantitative formation of **TbD**. On the other hand, 63% of deuterated phenylsilane derivative **1a** (E=D) was obtained along with 30% of **TbH** by D_2O addition at room temperature to an orange colloidal solution of the anion.

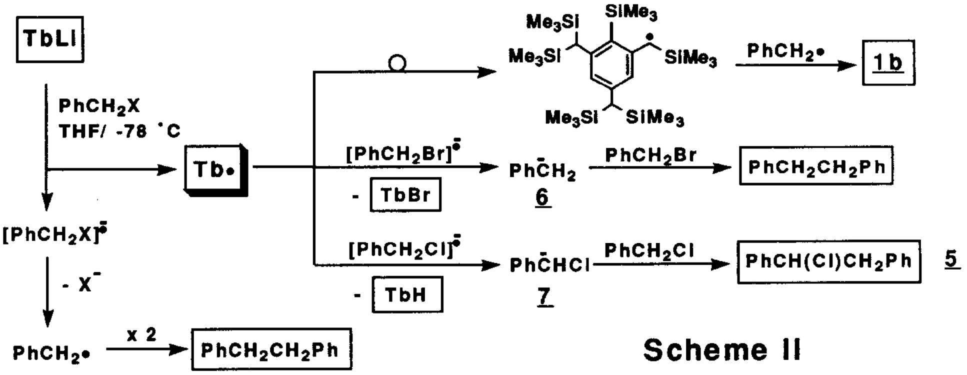


Scheme I

The formation of unusual rearranged product **1a** represents the first example of 1,3-anionic silicon rearrangement from carbon to carbon and is most likely interpreted in terms of the liability of a silicon atom to high-coordination leading to pentacoordinated silicon intermediate **3**. Since a 7:3 mixture of **TbH** and **TbD** (total 84%) was isolated together with 11% of **1a** by D_2O quenching at -20 °C, the 1,3-silicon rearrangement of **TbLi** is considered to compete with its proton abstraction reaction from THF leading to the **TbH** formation at the temperature range where the rearrangement becomes feasible.

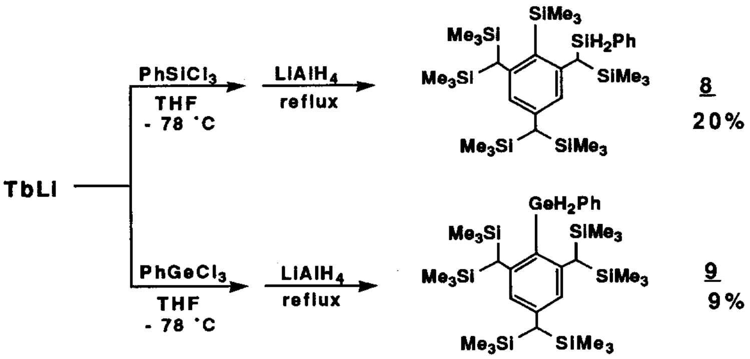


The rearranged benzyl anion **4** readily reacted with benzyl bromide at room temperature to give the corresponding coupling product **1b** ($E=CH_2Ph$)[7] in 78% yield together with **1c** (E=H, 3%)[8] and **TbH** (25%). On the contrary, treatment of the **TbLi** solution with benzyl bromide at -78 °C for 10 h followed by D_2O quenching at this temperature afforded unexpected products such as **1b** (4%), **TbD** (29%), **TbBr** (66%), and bibenzyl (28%). The reaction of **TbLi** with benzyl chloride under similar reaction conditions also gave **1b** (4%) along with a 9:1 mixture of **TbH** and **TbD** (total 94%), bibenzyl (7%), and 1-chloro-1,2-diphenylethane **5** (43%).



Scheme II

Taking account of the aforementioned stability of **TbLi** alone in THF even at -30 °C, the formation of the rearranged product **1b** by the treatment of **TbLi** with benzyl halides at -78 °C led us to propose an electron transfer reaction mechanism including the generation of **Tb** radical and its subsequent 1,3-silicon rearrangement and recombination with coexisting benzyl radical as shown in Scheme II. The formation of **TbBr** and bibenzyl derivatives is also consistently explained by further reactions of **Tb** radical with the counterpart anion radicals as shown in Scheme II, in which the relative stability of the resulting anions such as **6** and **7** and the higher reactivity of bromine than chlorine atom toward a radical are probably responsible for the dichotomy in the reaction pathway (*i. e.*, hydrogen *vs.* halogen abstraction).



Similar 1,3-silicon rearrangement product **8**[9] was obtained in 20% yield by treatment of **TbLi** with phenyltrichlorosilane followed by reduction using lithium aluminum hydride, while only the normal coupling product **9**[10] (9%) was isolated wihtout any amount of rearranged products in the case of phenyltrichlorogermane. The difference between $PhSiCl_3$ and $PhGeCl_3$ is probably due to the longer bond length of C-Ge than C-Si which allows the direct attack of **Tb** radical or anion to the germanium atom in spite of its steric bulkiness.

Acknowledgement: We are grateful to Shin-etsu Chem. Co. Ltd. for the gift of chlorosilanes. This work was partly supported by the Grant-in-Aid for Scientific Research (No. 02804039) from the Ministry of Education, Science, and Culture of Japan.

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7. **1b**; white crystals, mp. 118-119 °C; ^{1}H-NMR($CDCl_3$) δ -0.058(s, 9H), 0.014(s, 9H), 0.023(s, 9H), 0.073 (s, 18H), 0.19(s, 9H), 1.34(s, 1H), 2.17(s, 1H), 2.84(H_X, J_{AX} = 9.0 Hz, J_{MX} = 6.3 Hz, 1H), 2.96(H_M, J_{AM} = 13.8 Hz, J_{MX} = 6.3 Hz, 1H), 3.15(H_A, J_{AM} = 13.8 Hz, J_{AX} = 9.0 Hz, 1H), 6.32(brs, 1H), 6.66(brs, 1H), 7.00-7.16(m, 5H); ^{13}C-NMR($CDCl_3$) δ -1.47(q), 0.61(q), 0.78(q), 0.94(q), 6.05(q), 27.45(d), 30.16(d), 36.39(d), 40.06(t), 122.24(d), 125.76(d), 127.97(d), 128.01(d), 129.00(d), 129.56(s), 141.97(s), 143.23(s), 150.53(s), 152.34(s); MS, m/z 642(M^+, 5%), 481(7), 73(100); HRMS, m/z 642.3759, calcd for $C_{34}H_{66}Si_6$ 642.3779.

8. **1c**; white crystals, mp. 102-103 °C; ^{1}H-NMR($CDCl_3$) δ 0.014(s, 27H), 0.025(s, 18H), 0.36(s, 9H), 1.27 (brs, 1H), 2.19(brs, 1H), 2.25(s, 2H), 6.26(brs, 1H), 6.38(brs, 1H); ^{13}C-NMR($CDCl_3$) δ -0.55(q), 0.61(q), 0.71(q), 5.67(q), 27.26(d), 27.39(t), 29.70(d), 123.52(d), 127.31(d), 128.56(s), 142.96(s), 147.67(s), 150.03(s); MS, m/z 552(M^+, 12%), 537(2), 479(4), 464(8), 73(100); HRMS, m/z 552.3309, calcd for $C_{27}H_{60}Si_6$ 552.3309.

9. **8**; white crystals, mp. 90-92 °C; ^{1}H-NMR($CDCl_3$) δ 0.028(s, 9H), 0.036(s, 9H), 0.061(s, 9H), 0.078(s, 18H), 0.29(s, 9H), 1.33(s, 1H), 2.24(s, 1H), 2.38(t, J = 5.0 Hz, 1H), 4.53(d, J = 5.0 Hz, 1H), 4.57(d, J = 5.0 Hz, 1H), 6.30(brs, 1H), 6.65(brs, 1H), 7.23-7.44(m, 5H); ^{13}C-NMR($CDCl_3$) δ -0.19(q), 0.63(q), 0.73 (q),0.76(q), 5.93(q), 22.38(d), 27.34(d), 30.03(d), 122.74(d), 127.50(d), 127.82(d), 129.56(d), 133.22(s), 135.62(d), 143.73(s), 145.31(s), 149.50(s), 151.14(s); MS, m/z 658(M^+, 25%), 633(7), 585(35), 73(100); HRMS, m/z 658.3542, calcd for $C_{33}H_{66}Si_7$ 658.3548; these spectral data are undoubtedly different from those of $TbSiH_2Ph$ which can be synthesized by the nucleophilic phenyl substitution of $TbSiF_3$ followed by $LiAlH_4$ reduction.

10. **9**; white crystals, mp. 134-136 °C; ^{1}H-NMR($CDCl_3$) δ -0.03(s, 36H), 0.04(s, 18H), 1.32(s, 1H), 2.11(s, 2H), 5.14(s, 2H), 6.35(brs, 2H), 7.3-7.6(m, 5H); MS, m/z 704(M^+, 33%), 615(25), 552(33), 73(100); HRMS, m/z 704.2990, calcd for $C_{33}H_{66}Si_6Ge$ 704.2990.

(Received in Japan 4 January 1991)