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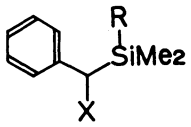
Effects of Si-Si σ-Bonds on Stability of Adjacent Benzylic Cations

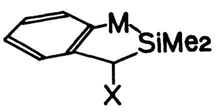
Nobujiro SHIMIZU,* Chieko KINOSHITA, Erika OSAJIMA, and Yuho TSUNO
Department of Chemistry, Faculty of Science, Kyushu University,
Hakozaki, Fukuoka 812

Solvolytic formation of α-pentamethyldisilanylbenzyl cation is about 7 kcal/mol energetically more favorable than that of α-trimethylsilylbenzyl cation from the corresponding bromides in 97% TFE.

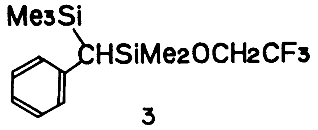
Si-Si single bonds possess unusually low ionization potentials1) and are capable of interacting with internal or external π systems.2) We report here quantitative estimation for the effect of Si-Si σ-bonds on stability of adjacent carbocations on the basis of solvolyses of α-pentamethyldisilanylbenzyl halides (**1a-Br** and **1a-Cl**) and 2,2,3,3-tetramethyl-2,3-disila-1-indanyl chloride (**2a-Cl**).3-5)



1a, R=SiMe3
b, R=Me
c, R=CMe3
d, α-methylbenzyl



2a, M=SiMe2
b, M=CH2



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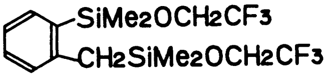

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The following observations characterize the effects of β-Si-Si σ-bonds. First, as shown in Table 1, **1a-Br** solvolyzed 1.89×10^{5} times more rapidly than α-trimethylsilylbenzyl bromide (**1b-Br**) in 97:3 (w/w) 2,2,2-trifluoroethanol(TFE)-water at 25 °C. Obviously, the β-$SiMe_2$-$SiMe_3$ σ-bond shows a remarkable rate-acceleration effect as compared to the β-$SiMe_2$-CH_3 σ-bond, although the overall effect of $SiMe_2SiMe_3$ is comparable to that of CH_3 due to the deactivating α-silicon effect.6) The steric effect of α-$SiMe_2SiMe_3$ relative to $SiMe_3$ can be estimated from a rate ratio of the structurally related substrates, **1c** and **1b**. A small rate ratio, k(**1c**)/k(**1b**)=0.44, observed for their tosylates indicates the effect of Si_2Me_5 to be mostly electronic in origin. Second, the solvolysis of **1a-Br** in TFE (and also in ethanol and aq. acetone) cleanly gave a 1,2-$SiMe_3$ rearranged

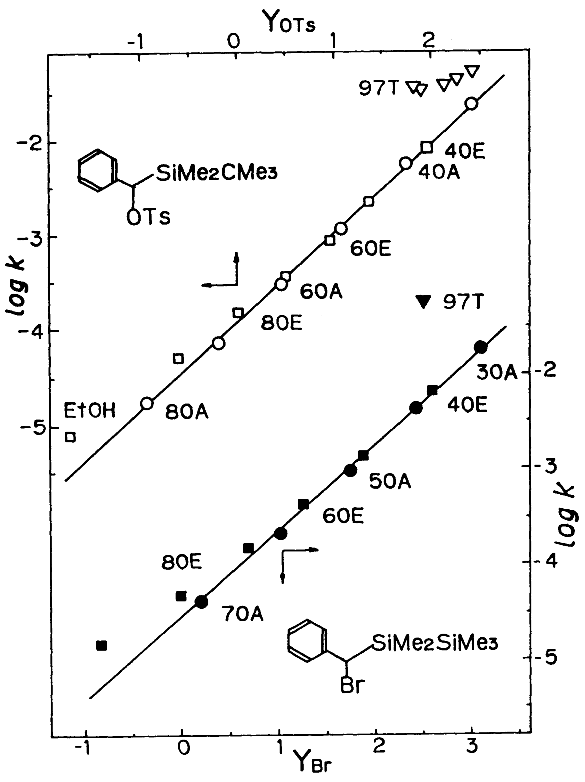
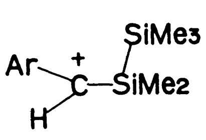


Fig. 1. mY-Plots for **1a-Br** (bottom) and for **1c-OTs** (top) in aq. acetone (-○-), aq. EtOH (-□-), and aq. TFE (-▽-).

product **3** in contrast to the absence of such a skeletal rearrangement in the solvolyses of **1b-OTs** and **1c-OTs**. Third, a cyclic substrate **2a-Cl** in which the Si-Si bond is orthogonal to the leaving group did not exhibit enhanced reactivity at all as compared to a reference compound **2b-Cl**; in fact, the former solvolyzed 4.8 times less rapidly than the latter in 97% TFE. Noteworthy is the formation of a structure-retained ether **2a-OTFE** as a major product (31%) besides a ring-opened compound **4**.

Figure 1 shows mY plots for the solvolyses of **1a-Br** and its β-alkyl analogue **1c-OTs** using the corresponding Y_{Br} and Y_{OTs} in EtOH-water, TFE-water, and acetone-water binary solvents. High m-values in aq. acetone solvents, 0.91 and 0.94 for **1a-Br** and **1c-OTs**, are indicative of rate-determining ionization in both cases. Close resemblance in their mY plots pattern strongly suggests that the transition state structure for the two substrates must be very close to each other irrespective as to whether the skeletal rearrangement is involved or not. The solvolysis of the chloride **1a-Cl** in 40% aq. ethanol showed a secondary α-D isotope effect of k_H/k_D=1.16, a value characteristic of the k_c solvolysis for α-methylbenzyl chloride (**1d-Cl**).[7] The rates of solvolysis of ring-substituted **1a-Cl** including p-Me, m-Me, H, p-Cl, and m-Cl groups in 40% aq. ethanol at 25 °C (k_1=1.10x10^{-2}, 8.52x10^{-4}, 5.96x10^{-4}, 2.36x10^{-4}, and 1.91x10^{-5} s^{-1}, respectively) were linearly analyzed by the Yukawa-Tsuno LArSR treatment[8] with a resonance parameter r=1.16 yielding a slope ρ=-3.71 (R=0.998). Although a small set of π-donor substituents might not lead an unambiguous r-value, the result is interestingly compared to the α-methylbenzyl solvolysis characterized by r = 1.15 and ρ around



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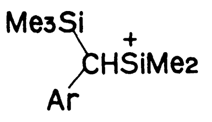

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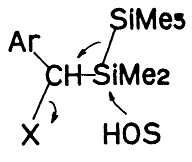

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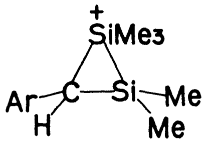

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Table 1. Solvolysis Rates for α-Disilanyl- and α-Silyl Substrates[a)]

Substrate	Solvent[b)]	k_1/s^{-1}	k_{rel}	m[c)]
1a-Br	97T	$5.92x10^{-2}$ d)	189,000	0.91
1b-Br	97T	$3.13x10^{-7}$ e)	1.0	
1d-Br	97T	$5.15x10^{-3}$	16,500	0.90
1b-OTs	40E	$1.79x10^{-2}$	1.0	0.91
1c-OTs	40E	$7.91x10^{-3}$	0.442	0.94
2a-Cl	97T	$3.86x10^{-4}$	0.210	
2b-Cl	97T	$1.84x10^{-3}$	1.0	0.98
1a-Cl	40E	$5.96x10^{-4}$ f)	1.0	0.98
1a-Cl-α-d$_1$	40E	$5.13x10^{-4}$ g)	0.861	

a) At 25 °C. b) 97T=97:3(w/w) 2,2,2-trifluoroethanol-water; 40E=40:60 (v/v) ethanol-water. c) m-Values were determined in three to six different acetone-water solvents ranging from 30% to 80% (v/v) mixtures using Y_{Cl}, Y_{Br}, and Y_{OTs} for chlorides, bromides, and tosylates. d) Extrapolated: $k_1=4.18x10^{-2}$, $1.90x10^{-2}$, and $8.71x10^{-3}$ s^{-1} at 20, 10, and 0 °C respectively. e) Extrapolated: $k_1=4.76x10^{-6}$ and $4.89x10^{-5}$ s^{-1} at 50 and 75 °C respectively. f) Average of triplicate runs. g) Average of duplicate runs.

-5.[9] An appreciable reduction in ρ-value for the α-disilanyl substrate suggests significant electron-donation from the β-Si-Si bond to the carbenium carbon. Thus, all these findings are consistent with the S_N1 mechanism involving the rate-determining formation of α-pentamethyldisilanylbenzyl cation **5** effectively stabilized by the adjacent Si-Si σ-bond mainly by hyperconjugation.[10] The cation decays to the rearranged product presumably via a silylenium ion **6**. A concerted mechanism (**7**) is clearly against the observations and the intervention of a siliconium ion intermediate **8** is untenable either.

The β-silicon effect by a factor of 10^5 relative to methyl in the present case is much smaller in magnitude than the rate-acceleration of 10^{12} by an anti-β-$SiMe_3$ group relative to hydrogen reported in the cyclohexyl solvolysis.[11] A direct comparison of these rate data, however, does not provide quantitative information on the relative effectiveness of the β-silicon effect in a C^+-Si-$SiMe_3$ system to that in a C^+-C-$SiMe_3$ system because of the different electron demand as well as the different conformational requirement in the benzylic and the cyclohexyl solvolyses.

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4) **1a-Br** and **1a-Cl** were prepared by treatment of benzyl bromide or chloride with LDA at -78 °C in the presense of $Me_3SiSiMe_2Cl$. **2a-Cl** was synthesized by the reaction of o-chloromethylphenyllithium with $ClMe_2SiSiMe_2Cl$ followed by a subsequent cyclization of the resulting o-(2-chlorotetramethyldisilanyl)benzyl chloride with LDA. All new compounds showed satisfactory spectral and analytical data. The following are representative. **1a-Br:** bp 98-99 °C (1 Torr; 1 Torr=133 Pa); NMR (CCl_4) δ=0.0 (9H, s), 0.13 (3H, s), 0.19 (3H, s), 4.32 (1H, s), 7.20 (5H, almost s). Anal. (C, 48.01; H, 6.96%). **2a-Cl:** bp 80-80.5 °C (0.5 Torr); NMR (CCl_4) δ=0.20 (3H, s), 0.31 (3H, s), 0.35 (3H, s), 0.41 (3H, s), 4.46 (1H, s), 7.08-7.65 (4H, m). Anal. (C, 54.80; H, 7.12%). **2b-Cl:** bp 125-126 °C (16 Torr); NMR (CCl_4) δ=0.22 (3H, s), 0.40 (3H, s), 1.99 (1H, d, J=17.4 Hz), 2.17 (1H, d, J=17.4 Hz), 4.30 (1H, s), 6.96-7.56 (4H, m). Anal. (C, 60.96; H, 6.61%).

5) The solvolyses were followed spectrophotometrically by measuring decrease of a reactant or increase of a producing acid as its acridinium salt and in several cases conductimetrically. In all cases, the solvolysis followed excellent first-order kinetics (R>0.9999).

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