Bull. Chem. Soc. Jpn., *72*, *1043—1047 (1999)* 1043

The γ-Silicon Effect. II.[1]
The Substituent Effect on the Solvolysis of 3-(Aryldimethylsilyl)-2,2-dimethylpropyl *p*-Bromobenzenesulfonates

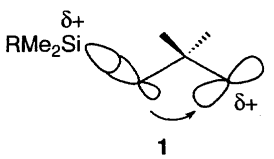
Tohru Nakashima, Ryoji Fujiyama,* Mizue Fujio,* and Yuho Tsuno

Institute for Fundamental Research of Organic Chemistry, Kyushu University, Hakozaki, Fukuoka 812-8581

(Received September 29, 1998)

Solvolysis rates of 3-(aryldimethylsilyl)-2,2-dimethylpropyl *p*-bromobenzenesulfonates were determined in 60% (v/v) aqueous ethanol (60E) and 97% (w/w) aqueous 2,2,2-trifluoroethanol (97Tw) at 50 °C. The effects of aryl substituents at the silyl atom on these solvolyses were correlated with unexalted σ° parameters, giving the ρ values of -0.87 in 60E and -1.08 in 97Tw. This indicates that there exists a certain extent of positive charge on the γ-silicon atom reflecting the delocalization of incipient carbocationic charge by participation of the Si–C_γ bond. The size of ρ values can be regarded as the effect of aryl ring on γ-Si via percaudal interaction in the rate-determining step.

The rate acceleration by silicon substituents at the γ position to the cationic reaction center is designated as the γ-silicon effect.[2,3] The γ-silicon substituent facilitates ionization, especially when the silyl group has a particular geometrical orientation with respect to the leaving group; i.e., a "W" conformation is needed for the kinetic γ-silicon effect. The mechanism involves the formation of a carbocation (**1**) stabilized by the γ-silyl group through the so-called percaudal interaction, in which the back lobe of the Si–C_γ bond overlaps with the developing vacant p-orbital on the cationic center (Scheme 1).[2,3] Recently, we have reported the solvolyses of 2,2-dimethyl-3-(trimethylsilyl)propyl and 3-(aryldimethylsilyl)-2,2-dimethylpropyl tosylates (OTs; *p*-toluenesulfonates) (**2**) which showed large rate accelerations of 10^3—10^4 compared with the γ-H derivative, neopentyl OTs.[1] The solvent effects on these γ-silyl-assisted solvolyses have been analyzed by using the Winstein–Grunwald equation. The results demonstrate a significant degree of the delocalization of developed cationic charge by the γ-silyl group via the assisting Si–C_γ bond in the transition state (**4**) (Scheme 2).[1] Products were derived exclusively from the tertiary cation **5**, which is formed by rearrangement of the (aryldimethylsilyl)methyl group.[1] These results were in line with the rate-determining formation of **4** stabilized by the γ-silyl group. In order to obtain further evidence for charge delocalization into the γ-silyl group occurring through percaudal interaction, we investigated the substituent effect on this reaction; the substituent effect should reflect the delocalization of cationic charge in the bridged transition state **4**.



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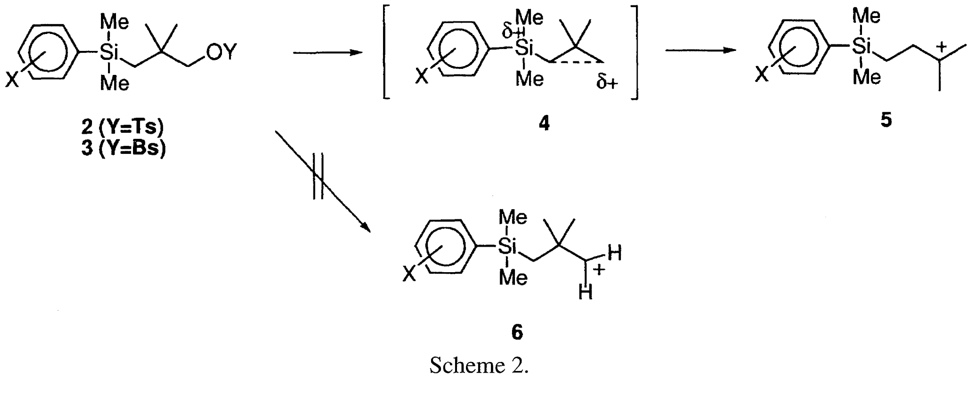
Scheme 1.

The Yukawa–Tsuno (Y–T) Eq. 1 is one of the most useful tools to predict the specifics of a transition state whose reaction center is affected by benzene π-system:[4,5]

$$\log(k/k_\circ) = \rho(\sigma^\circ + r\Delta\overline{\sigma}_R^+), \tag{1}$$

where k is the rate constant for a given reaction of a ring-substituted derivative and $k_\circ$ is the corresponding value of the



Scheme 2.

unsubstituted one. Symbol σ° is the normal substituent constant which involves no additional π-electronic interaction between the substituent and the reaction center, and $\Delta\overline{\sigma}_R^+$ is the resonance substituent constant, defined by $\sigma^+ - \sigma^\circ$, measuring the capability for π-delocalization of *p*-π-donor substituent. The solvolysis of 1-methyl-1-phenylethyl chlorides is the σ^+ defining system which is the reference standard of $r = 1.00$ in the Y–T Eq. 1.[4—6] In this equation, the *r* value is the parameter measuring the degree of resonance interaction between the carbocationic center and benzene π-system. The Y–T Eq. 1 has been applied successfully to the analysis of various benzylic solvolyses; the ρ and *r* values permit the evaluation of the nature of the transition state.[4,5]

While the kinetic effect (i.e., reactivity change) of the silyl-displacement of carbon should be a measure of the significance of particular silicon effects, the selectivity effects (i. e., change in ρ and/or *r*) for the silyl function should be a much more important probe for evaluation of the nature of transition state. Accordingly, in order to clarify the percaudal interaction mechanism, we have carried out the analysis of the aryl substituent effect on the γ-Si atom in the solvolysis of 3-(aryldimethylsilyl)-2,2-dimethylpropyl brosylates (OBs; *p*-bromobenzenesulfonates) (**3**).

Results and Discussion

Solvolysis rates of **3** were determined for widely varying substituents (*p*-MeO, *p*-Me, *m*-Me, H, *p*-Cl, *m*-Cl, and *m*-CF_3) in 60% (v/v) aqueous ethanol (60E) and 97% (w/w) aqueous 2,2,2-trifluoroethanol (97Tw) at 50 °C. Data are summarized in Table 1. The rate change with ring substituents was fairly small in both solvents; only ca. 4 fold for a wide range of substituent changes from the *p*-MeO to *m*-CF_3.

Table 1. Rate Constants for Solvolyses of 3-(Aryldimethylsilyl)-2,2-dimethylpropyl Brosylates at 50 °C

	$10^5 \times k_t/s^{-1}$ a)	
Subst.	60E[b)]	97Tw[c)]
p-MeO	15.5	64.7
p-Me	16.0	73.3
m-Me	13.1	64.1
H	12.8 (7.612)[d)]	52.7 (35.87)[d)]
H(OTs)	(1.378)[e)]	(11.03)[e)]
p-Cl	7.95	26.2
m-Cl	5.28	19.2
m-CF_3	4.35	15.6

a) The reproducibility of the rate constants is within ±1.5%. b) 60% (v/v) aqueous ethanol. c) 97% (w/w) aqueous 2,2,2-trifluoroethanol. d) At 45 °C. e) Tosylate at 45 °C, taken from Ref. 1.

The brosylate/tosylate rate ratio for unsubstituted derivative is a constant of 5.5 in 60E and 3.3 in 97Tw, as shown in Table 1, and the change in these leaving groups does not affect results of the substituent effect.

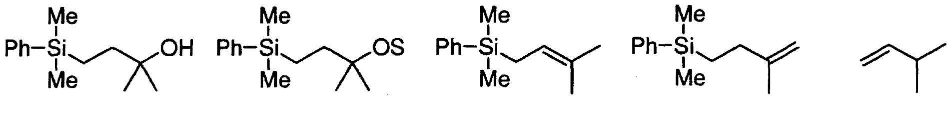
The result of products from the unsubstituted derivative of **3** is given in Scheme 3. As reported in the previous paper,[1] the products from **2** in 70% (v/v) aq acetone (70A) at 55 °C were almost identical regardless of the aryl substituents on the γ-silicon atom. The products from the brosylate **3** in 70A in Scheme 3 were essentially the same as those from the tosylate **2** in 70A in the previous paper, while the product ratios were dependent slightly on the solvent. Products were derived exclusively from the tertiary cation **5**, formed through the migration of γ-Si group, and no solvent-substituted product at the primary center was observed, thereby excluding an S_N2 displacement reaction. These are in line with the rate-determining formation of the carbocation (or transition state) **4** stabilized by the γ-silyl group (Scheme 2).

Regardless of the large difference in solvent nucleophilicity (N_{OTs}) between 97Tw (−2.79) and 60E (−0.09),[7] the substituent effects in both solvents are almost the same; there exists a linear relation ($R = 0.990$, SD = ±0.04) with approximately unit slope between the two logarithmic rates for substituent changes.

$$\log (k/k_o)_{97Tw} = 1.22 \log (k/k_o)_{60E}.$$

This fact can exclude an occurrence of the S_N2 displacement mechanism and is also consistent with the absence of solvent-substituted products at the primary reaction center. The rate of the *p*-MeO derivative is slower than that of the *p*-Me derivative, indicating that the substituent effect on this solvolysis can be characterized as the resonance unexalted σ° reactivity ($r \cong 0$). As shown in Figs. 1 and 2, the logarithms of the relative rates were correlated directly with σ°, giving ρ values of −0.87 in 60E ($R = 0.992$ and SD = ±0.03) and −1.08 in 97Tw ($R = 0.9993$ and SD = ±0.01). In fact, an application of Y–T Eq. affords good correlations with $r \cong 0$; $\log (k/k_o) = (-0.85 \pm 0.06)(\sigma^\circ + (0.05 \pm 0.07)\Delta\overline{\sigma}_R^+)$ ($R = 0.993$ and SD = ±0.03) for 60E and $\log (k/k_o) = (-1.10 \pm 0.01)(\sigma^\circ + (-0.03 \pm 0.01)\Delta\overline{\sigma}_R^+)$ ($R = 0.9998$ and SD = ±0.007) for 97Tw.

The small but negative ρ values obtained demonstrate that a significant amount of positive charge resides on the Si atom at the γ position. The *r* value of 0.0 assigned for this system



60E	24%	12% (S=C_2H_5)	49%	12%	3%
97Tw	8%	20% (S=-CH_2CF_3)	47%	7%	18%
70A	35%	-	51%	13%	1%

Scheme 3. Product analysis.

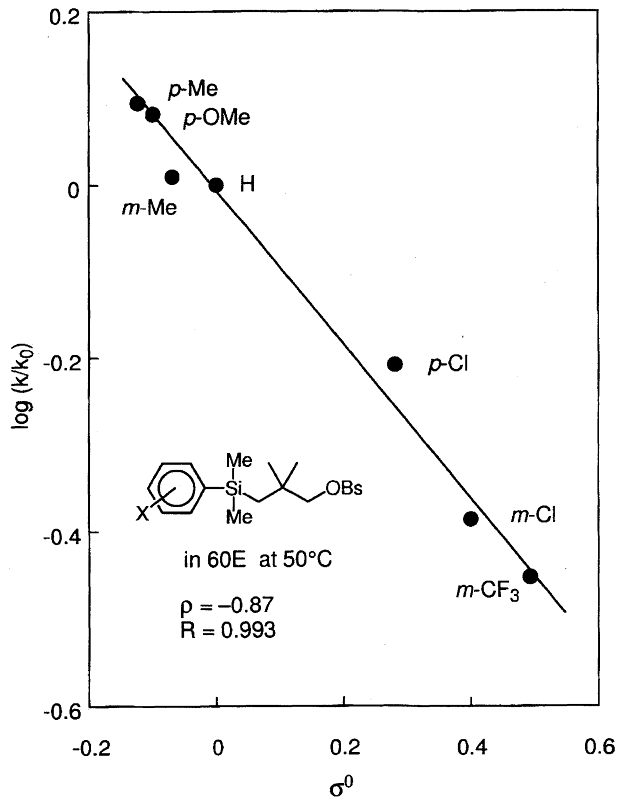


Fig. 1. Hammett plot for the solvolysis of 3-(aryldimethylsilyl)-2,2-dimethylpropyl brosylates in 60% (v/v) aqueous EtOH at 50 °C.

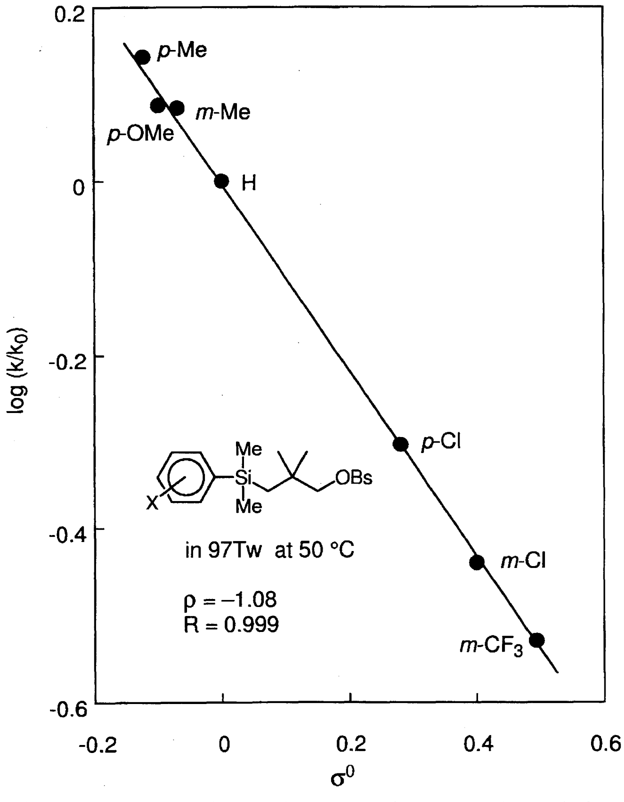


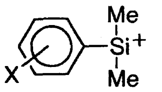
Fig. 2. Hammett plot for the solvolysis of 3-(aryldimethylsilyl)-2,2-dimethylpropyl brosylates in 97% (w/w) aqueous 2,2,2-trifluoroethanol at 50 °C.

may be explicable if the phenyl π-system on the γ-silicon atom interacts through the Si–C σ-bond only indirectly (by non-π-interaction mechanism) with the carbocationic reaction center in **4**.

In our previous work,[1] the solvent effect for this γ-silicon system leads to the conclusion that the solvolysis of **2** should be the generation of a carbocation intermediate, independent of the nucleophilic solvent assistance. The rate-determining formation of open cation **6** is also evidently denied, from the fact that the absolute value of ρ obtained is too large to be the value for the γ-aryl group remote from the reaction center in **6** even when taking into account the attenuation of substituent effect through C–C bond. It is, therefore, quite reasonable that ρ of -1.0 for the present solvolysis is taken as the effect of the γ-Si assisting transition state **4**.

The effects of aryl substituents on the positive charge formation at the silicon atom have rarely been investigated, since it is so difficult to generate a silyl cation intermediate under the solvolysis conditions,[3] while those for the carbocation system have been studied extensively.[5] The substituent effect on the formation process of the silyl cations in the solution has been recently reported by Mayr and co-workers, who measured rates of hydride-transfer reaction from (*para*-substituted phenyl)dimethylsilanes to diarylcarbocation in dichloromethane solution at −70 °C.[8] The aryl substituent effect on the rate-determining formation of aryldimethylsilyl cations (**7**) was linearly correlated with σ ($r = 0.27$) to give $\rho = -2.46$ (Chart 1).[8] On the other hand, the substituent effect on the solvolysis of 1-methyl-1-phenylethyl chloride was $\rho = -4.56$ and $r = 1.00$ in 90% aq acetone at 25°C.[5,6] The ρ and r values for the silyl cation **7** were remarkably smaller than those for the carbon analogue, 1-methyl-1-phenylethyl cation (**8**). The same behavior was observed for thermodynamic stabilities of cations **7** and **8** in the gas phase. An application of the Y–T Eq. to the substituent effect on the gas phase cation **7** gave ρ of -5.87 and r of 0.29[9] which are distinctly smaller compared with the ρ of -9.5 and $r = 1.00$ for the gas-phase carbocation **8**.[10] The r value for the silyl cation in the gas phase is identical with that in solution. These results indicate that cationic charge on a silicon atom does not have large demand for the polar and resonance effects compared with the carbon analogue.

Even if the positive charge is fully developed at the silicon atom in the silyl cation **7**, the substituent effect can be characterized by the very small ρ and r values compared with those for the carbon analogue. On the other hand, the identity of the r value between the gas phase cation formation and the corresponding solvolysis, as observed for many benzylic cation systems, holds also in the case of the silyl cation, while the ρ value in the solution phase is reduced more significantly,



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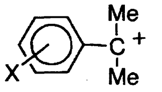

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Chart 1.

to almost one half of that in the gas phase, due to charge dispersion by the solvation.[5] Accordingly, we can estimate the ρ value to be about -2.9 for the solvolysis leading to the aryldimethylsilyl cation **7** from the substituent effect in the gas phase. This estimated ρ value is in good agreement with the $\rho = -2.5$ observed for the hydride-transfer reaction leading to the silyl cation **7** in dichloromethane, even though the ρ value is appreciably dependent on temperature or solvent. Thus, the substituent effect on the hydride-transfer reaction of **7** should be the effects of aryl ring substituents at the Si where the positive charge is almost fully developed in the transition state.

The solvolyses of 2-(trimethylsilyl)ethyl bromide and 2-(aryldimethylsilyl)ethyl chlorides gave the deuterium scrambling in the ethyl chain for the former system[11] and the aryl substituent effects of $\rho = -1.2$—-2.3 with σ constant for the latter.[12,13] In the solvolyses of β-(arylsilyl) precursors **9**, $ArSiMe_2$–$CH(Me)CH_2$–ODNBz (3,5-dinitrobenzoate) or $ArSiMe_2$–$C(Me)_2CH_2$–ODNBz, appreciably high ρ values, -1.8—-1.5,[14] have been obtained. These should be ascribed to the reflection of the silyl-participation to the carbocation center in the transition state (Scheme 4). Taking the attenuation coefficient of ρ parameter to be as a general rule ca. 1/2 for an intervening bond,[15] one would expect the cationic center in the transition state to be at the atomic position next to the silyl atom. This is consistent with bonding (silyl-participation) between Si and β-carbocation center in the transition state of **10**. It is all the more remarkable that the α-phenyl or α-*t*-butyl derivatives of **9** where no silyl-participation is involved gave a distinctly low ρ value of -0.9—-1.0,[14] which should be referred to as the normal ρ value for the effects of aryl substituents on the β reaction center of open chain **11** (Scheme 4).

The reduced ρ value of -1.0 for **3** is of course due to the long distance between aryl substituent and the reaction center in the transition state, and should be interpreted in terms of the structure of the transition state **4**, by taking into account the attenuation of the ρ value due to the number of intervening bonds.

The ρ value obtained for **3** where the reaction center is located at the γ position from the silyl function, is identical with the ρ value expected for the reaction center at the β-position from the silyl function as in **9**. The absence of attenuation of ρ for the increased number of intervening bonds (from **9** to **3**) can be most reasonably attributed to the contraction of the chain by the percaudal interaction in the transition state **4**. Although the percaudal interaction in the present system is evidenced by exclusive production of rearranged products derived from **5** instead of direct displacement ones via **6**, the loss of attenuation in the ρ value indicates that the bonding is substantial in the percaudal interaction in the transition state **4** in the present system.

Experimental

Materials. 3-(Aryldimethylsilyl)-2,2-dimethyl-1-propanols were prepared as previously reported and converted to the brosylates in the same procedure as the tosylates.[1] To the solution of the lithium alkoxide prepared from the above alcohol and 1.6 M butyllithium in ether (1 M = 1 mol dm^{-3}) was added *p*-bromobenzenesulfonyl chloride at 0 °C, and the mixture was stirred overnight. After the usual work-up, the brosylate was purified by SiO_2 column chromatography. All brosylates were colorless liquids. The elemental analyses agreed well with the established values (Table 2).

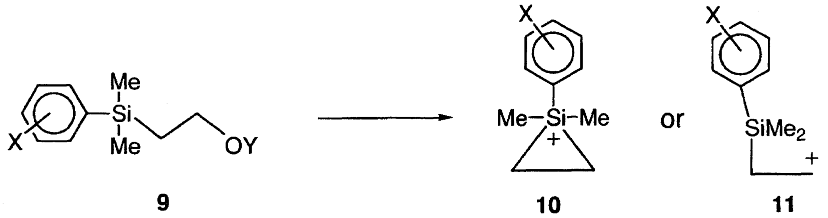
Solvents. Solvents were purified as previously described[1,7] and binary solvents prepared by mixing appropriate volumes or weights of pure solvents at 25 °C.

Kinetic Measurements. Solvolyses in binary solvent mixtures were followed conductimetrically.[1,7] We used a conductivity meter (CM-50AT and CM-60S, Toa Electronics Ltd.) equipped with an interval time unit and printer to follow the solvolyses in a thermostatted bath controlled at 50±0.01 °C. At least 40 readings were taken at appropriate intervals during 4 half-lives, and all kinetic runs were followed over 95% completion. The experimental errors in respective runs were generally less than 1.0% and the reproducibility of the rate constants was within ±1.5%.

Product Analyses. Product analyses for the unsubstituted compound were carried out according to the same procedure as the tosylates described before.[1] A 1.9—3.5×10^{-2} M solution of the brosylate buffered with 4.2—7.6×10^{-2} M of 2,6-lutidine in deuterated 60E, 97Tw, and 70A was allowed to react at 75 °C for ten half-lives. The solvolysis products were identified by comparing their ^1H NMR spectra with those of authentic samples. The relative amounts of reaction products were determined from the integral areas of the corresponding peaks. The results are summarized in Scheme 3.

Table 2. Analytical Data of 3-(Aryldimethylsilyl)-2,2-dimethylpropyl Brosylates

Substituent	Carbon/%		Hydrogen/%	
	Found	Calcd	Found	Calcd
p-MeO	50.83	50.95	5.75	5.77
p-Me	52.64	52.74	5.97	5.98
m-Me	52.92	52.74	6.17	5.98
H	51.53	51.70	5.65	5.71
p-Cl	48.03	47.95	5.11	5.08
m-Cl	48.11	47.95	5.33	5.08
m-CF_3	46.87	47.15	4.79	4.75



Scheme 4.

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