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The γ-Silicon Effect. III.[1] The Yukawa-Tsuno Treatment in the Solvolysis of 2-Aryl-3-(trimethylsilyl)propyl Tosylates

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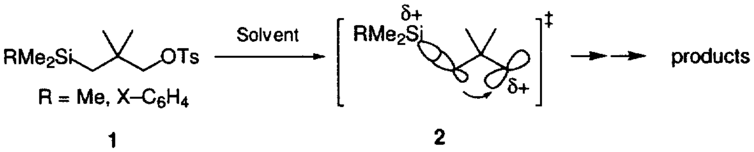
Abstract: Solvolysis of 2-aryl-3-(trimethylsilyl)propyl tosylate revealed the competitive assistances of the β-aryl and β-(trimethylsilyl)methyl groups. It is found out that the enhanced reactivity by the percaudal interaction of trimethylsilylmethyl group is comparable with that by π-participation of β-phenyl group, and is extraordinarily larger than that by σ-participation of the alkyl group.

Keywords: Mechanisms; Solvolysis; Silyl compounds; Substituent effects; Linear free energy relationship

The solvolysis of propyl sulfonates is greatly accelerated by γ-silyl substituents especially when the Si-C$_\gamma$ bond and C-O bond of the leaving group are disposed in a planar W-conformation (Scheme 1).[2-5] The so-called γ-silicon effect is due to the interaction of the back lobe of the Si-C$_\gamma$ bond with the developing vacant p-orbital on the cationic center (percaudal interaction).[2-5]



Scheme 1

We recently reported that the solvolyses of 2,2-dimethyl-3-(trimethylsilyl)propyl and 2,2-dimethyl-3-(aryldimethylsilyl)propyl tosylates (**1**) exhibited large rate accelerations (10^3 – 10^4) due to the formation of the γ-silyl stabilized carbocation with concomitant migration of the (RMe$_2$Si)methyl group.[1] Solvent effects were evaluated by the Winstein-Grunwald Eq. and were found to be similar to those observed for the k_Δ solvolyses of various β-arylalkyl systems. However assistance by the Si-C$_\gamma$ bond was less than half that obtained for *p*-MeO-neophyl solvolysis where the positive charge is strongly delocalized into a bridged phenonium ion.[1]

To measure quantitatively the charge delocalization by the percaudal interaction, we decided to study the solvolysis of 2-(substituted phenyl)-3-(trimethylsilyl)propyl tosylates (**3**) where participation by the aryl and Si-C$_\gamma$ groups should compete with each other. The solvolysis rates of **3** were determined conductimetrically in 50% (v/v) aq. acetone (50A) at 75°C (Table 1).[1]

Product analyses were carried out in 50% (v/v) $(CD_3)_2CO$-D_2O in the presence of excess 2,6-lutidine at 75°C by ^1H NMR spectroscopy (Table 1), as described before.[1] The products formed arose exclusively by rearrangement of the aryl and trimethylsilylmethyl(TMSM) groups. No substitution at the primary center by solvent was observed. Assuming the products to be entirely kinetic, the overall rate constant k_t can be partitioned between k_{Ar} and k_{Si} (Table 1); $k_t = k_{Ar} + k_{Si}$ (Scheme 2).

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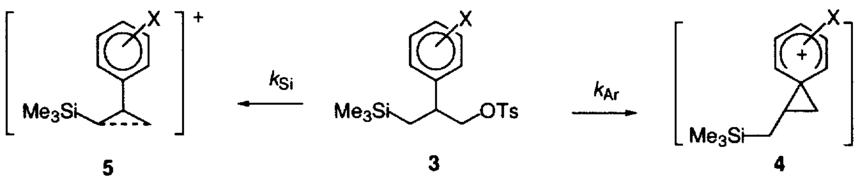


Scheme 2

The effect of substituents on aryl-assisted solvolyses of β-arylalkyl tosylates or β,β-diarylethyl tosylates can be successfully analyzed by the Yukawa-Tsuno (Y-T) Equation (Eq. 1),[6-9]

$$\log (k/k_o) = \rho(\sigma^o + r\Delta\bar{\sigma}_R^+) \qquad (1)$$

where σ^o is the normal substituent constant, which involves no additional π-electronic interaction between the substituent and reaction center; $\Delta\bar{\sigma}_R^+$ is the resonance substituent constant measuring the capability for π-delocalization of the *p*-π-electron-donor substituent, defined by $\sigma^+ - \sigma^o$.[6] The r value is a parameter characteristic of a given reaction, measuring the degree of resonance interaction between the aryl group and the reaction site in the rate-determining step.

Substituent effects for the solvolysis of **3** are obtained by plotting the logarithms of the relative rates against σ^+ (open circles), σ^o (closed circles), and σ_Δ (open squares) for r = 0.57 derived from the neophyl system[7] (Fig. 1). It is seen that these correlations are non-linear. The concave curve for the overall solvolysis rates is similar to that observed for the solvolysis of the 2-phenylethyl or *threo*-3-aryl-2-butyl system[8] and indicates that a mechanistic change occurs when the substituents vary. In other words, the non-linearity seen with σ_Δ indicates a gradual switch from the aryl-assisted to the TMSM-assisted mechanism when the aryl substituents are varied from an electron-donating to an electron-withdrawing group.

On the other hand, the dissected partial rate constants for aryl-migration (k_{Ar}) plotted against $\bar{\sigma}$ for r = 0.54 give a straight line (the open diamond plots in Fig. 1). The substituent effect is described with excellent precision (R=0.999) by Eq. 2.

$$\log (k/k_o)_{Ar} = -3.72(\sigma^o + 0.54\Delta\bar{\sigma}_R^+) \qquad (2)$$

The exalted r value can be rationalized in terms of a direct π-interaction between the aryl π-system and the β-

Table 1. Rate constants and product ratios obtained for solvolysis of **3** in 50%(v/v) aq. acetone at 75°C

Subst.	P_{Ar}/P_{Si}[a]	10^5k_t (s^{-1})[b]	10^5k_{Ar}(s^{-1})[c]	10^5k_{Si}(s^{-1})[d]
p-MeO	96/4	140.8	135.2	5.6
p-Me	75/25	20.37	15.28	5.09
m-Me	46/54	8.137	3.743	4.394
H	38/62	6.177	2.347	3.830
p-Cl	17/83	2.396	0.407	1.989
m-Cl	6/94	1.404	0.084	1.320
m-CF_3	3/97	0.969	0.029	0.940

[a] P_{Ar} = % of aryl-rearranged products including of 3-arylpropene. P_{Si} = % of silyl-rearranged products including arylcyclopropane. In 50% $(CD_3)_2CO$-D_2O in the presence of 2,6-lutidine. At 75°C. [b] Overall rate constants (±1.5%) in 50% aq. acetone at 75°C. [c] $k_t \times P_{Ar}/100$. [d] $k_t \times P_{Si}/100$

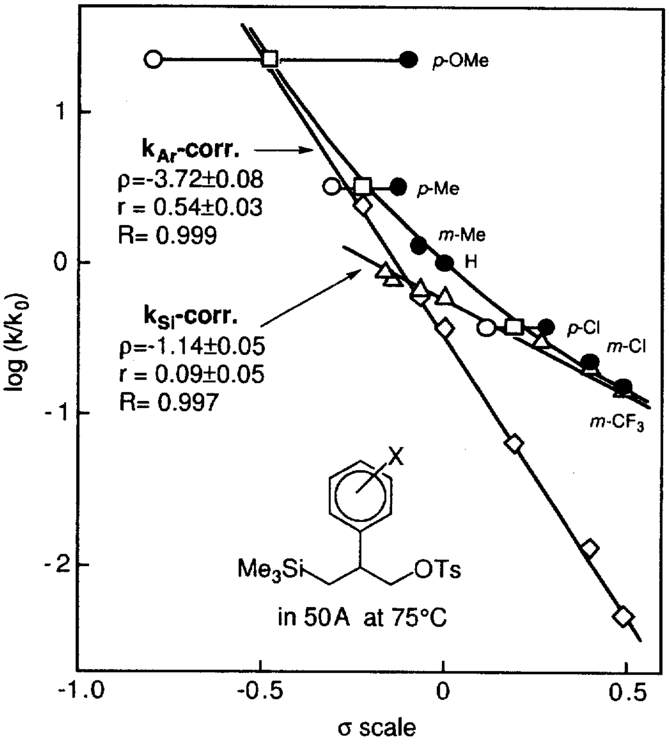


Fig. 1. Substituent effects on the solvolysis of 2-aryl-3-(trimethylsilyl)propyl tosylates in 50A at 75°C; σ^+ (open circles), σ^o (closed circles), and σ_Δ (i.e., $\bar{\sigma}$ for r = 0.57, open squares). The open diamonds are the Y-T plots for the dissected aryl-assisted process ($\bar{\sigma}$ for r = 0.54) and triangles for the TMSM-assisted process ($\bar{\sigma}$ for r = 0.09).

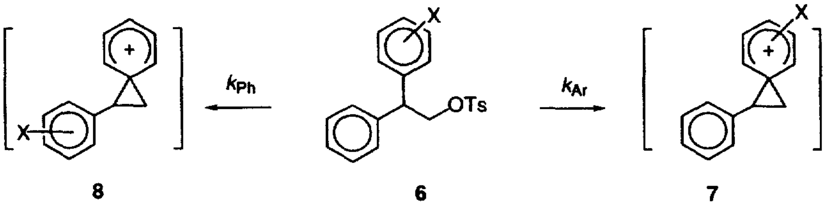
carbocation center at the rate-determining step, and large negative ρ value is in agreement with the aryl-bridged transition state.

The substituent effect on the partial rates for the TMSM-migration (k_{Si}) also exhibits an excellent linear Y-T correlation (the open triangles in Fig. 1), giving a ρ = −1.1 and an r value of 0.09.

$$\log (k/k_o)_{Si} = -1.14(\sigma^o + 0.09\Delta\bar{\sigma}_R^+) \qquad (3)$$

The k_{Si}-correlation (3) with a small ρ value and an essentially unexalted σ^o scale is compatible with the Si-Cγ bridged transition state.

The above results are in agreement with the reaction scheme 2 for the solvolysis of **3**, i.e., the competitive formation of the TMSM-bridged **5** and aryl-bridged **4** carbocations. The correlations of substituent effects, not only the apparent correlation as in Fig. 1 but also those for respective processes (Eqs. 2 and 3), are essentially identical to the corresponding ones for the solvolysis of the β,β-diarylethyl system (**6**) in Scheme 3,[9] where the TMSM group in Scheme 2 is replaced by a phenyl group.



Scheme 3

Both **3** and **6** systems appear to occur via the same reaction scheme, by the competition of aryl-assisted and aryl-unassisted processes, and more important, they show the same substituent effect correlations for the two processes. The large identical ρ and r values for **3** → **4** and **6**→**7** indicate the importance of the effect of substituents at the bridging aryl group whereas the small ones for **3** → **5** and **6**→**8** are indicative of negligible effects of substituents in the unbridging aryl group. The mechanistic changeover between two processes caused by the ring substituents in the solvolysis of **3** can be related to how effective the γ-silyl-assistance and aryl-assistance.

In the aryl-assisted pathways, **3** → **4** and **6**→**7**, the unassisting TMSM group shows a 5-hold rate-enhancement (non-percaudal effect) compared with the unassisting phenyl group, and the rate enhancement of the unassisting β-alkyl group is known to be only 1.3 hold. It is therefore remarkable that the reactivity-enhancement by the percaudal interaction of silylmethyl group in **5** (X=H) is comparable with that by π-participation of β-phenyl group in **4** (X=H), and is remarkably larger (by more than 10^4)[1] than that by σ-participation of the alkyl group.

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