Anchimeric Assistance by γ -Aryl Groups in Solvolysis of Organosilicon lodides. Some Remarkably Large Remote Substituent Effects

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The very large spread of rates in reactions of the iodides $(Me_3Si)_2C(SiMe_2C_6H_4X)(SiMe_2I)$ (X = *p*-OMe, *p*-Me, H, *p*-CI, or *m*-CF₃) with $(CF_3)_2CHOH$ and CF_3CH_2OH (the compound with X = *p*-OMe is 1.9×10^5 and 6.5×10^4 times, respectively, as reactive as that with X = *m*-CF₃) is attributed to nucleophilic assistance by the aryl group to the leaving of the I⁻ ion.

It was shown previously that in reactions of the iodides (Me₃Si)₃C(SiR₂I) with electrophiles, such as Ag^I salts or trifluoroacetic acid, rearranged products of the type (Me₃- $Si_2C(SiR_2Me)(SiMe_2Y)$ can be formed exclusively (e.g. R = Ph or Et along with unrearranged products (Me₃Si)₃C-(SiR₂Y), apparently via a cation of the type [(1), Z = Me].¹ Analogous 1,3-migration of a vinyl group was observed in the reaction of (Me₃Si)₂C(SiMe₂CH=CH₂)(SiEt₂I) with silver salts, and the much greater ease of reaction of the iodide $(Me_3Si)_2C(SiMe_2CH=CH_2)(SiMe_2I)$ than of $(Me_3Si)_3C$ -SiMe₂I toward CF₃CH₂OH or CF₃CO₂H was attributed to nucleophilic assistance by the vinyl group to the rate-determining departure of the iodide ion to form the cation [(1), R =Me, $Z = CH=CH_2$.² The corresponding 1,3-migration of the Ph group was recently observed in the reaction of (Me₃- $Si_2C(SiMe_2Ph)(SiEt_2I)$ with Ag^I salts, and attributed to formation of the cation [(2), R = Et, X = H].³

That observation did not, however, show that the aryl group participated in the rate-determining step, and an earlier attempt to detect such participation in the reactions of the related iodide $(Me_2PhSi)_3CSiMe_2I$ gave ambiguous results.⁴ We have now demonstrated beyond reasonable doubt that the aryl groups in $(Me_3Si)_2C(SiMe_2C_6H_4X)(SiMe_2I)$ can provide powerful anchimeric assistance in alcoholysis.

The iodides were made (in low yields) by the route shown in Scheme 1. Rate constants were determined by ¹H n.m.r. spectroscopy for their reactions with (CF₃)₂CHOH and CF₃CH₂OH, both of which can provide strong electrophilic assistance to the leaving of the iodide ion. (For the exact compositions of the media see the footnotes to Table 1; some CDCl₃ was present to ensure dissolution of the iodide and Et₃N to prevent cleavage of the Si–aryl bonds by formed HI.) Observed first-order rate constants, k, and relative rate constants, k_{rel} , are shown in Table 1. The product from the reaction with CF_3CH_2OH was the expected alkoxide (Me₃-Si)₂C(SiMe₂C₆H₄X)(SiMe₂OCH₂CF₃), but that from reaction with (CF₃)₂CHOH was the hydroxide, (Me₃Si)₂C-(SiMe₂C₆H₄X)(SiMe₂OH), presumably formed from traces of water, which competes successfully with (CF₃)₂CHOH for the intermediate cation because of the bulk and low nucleophilicity of this alcohol.

The features of the results, and suggested explanations, are

Table 1. Observed (k) and relative (k_{rel}) first-order rate-constants, m reactions of the iodides $(Me_3Si)_2C(SiMe_2C_6H_4X)(SiMe_2I)$ with ROH at 35 °C.

	$\mathbf{R} = (\mathbf{CF}_3)_2 \mathbf{CH}^{\mathbf{a}}$		$R = CF_3CH_2^b$	
Х	$10^{6} k/s^{-1}$	k _{rel}	$10^{6} k/s^{-1}$	k _{rel}
p-OMe	3.05×10^{3}	151	1.40×10^{3}	80
p-Me	6.3×10^{2}	31	$1.65 imes 10^2$	9.4
H	2.02×10	1.00	1.75×10	1.00
p-Cl	3.7×10^{-1}	$1.8 imes10^{-2}$	$8.5 imes 10^{-1}$	4.9×10^{-2}
m-CF ₃	1.58×10^{-2}	$7.8 imes 10^{-4}$	$2.17 imes 10^{-2}$	1.24×10^{-3}

^a A solution of 5—10 mg of the iodide and *ca*. 2 mol. equiv. of Et_3N in 600 µl of CDCl₃ was mixed with 200 µl of (CF₃)₂CHOH. ^b As footnote a, but with 400 µl of CDCl₃ and 500 µl of CF₃CH₂OH.



$$(Me_{3}Si)_{2}CCl_{2} \xrightarrow{i, ii} (Me_{3}Si)_{2}C(Cl)(SiMe_{2}C_{6}H_{4}X)$$

$$\downarrow i, iii$$

$$(Me_{3}Si)_{2}C(SiMe_{2}C_{6}H_{4}X)(SiMe_{2}I) \xleftarrow{iv} (Me_{3}Si)_{2}C(SiMe_{2}C_{6}H_{4}X)(SiMe_{2}H)$$

Scheme 1. Reagents and conditions: i, Bu^pLi in tetrahydrofuran–Et₂O–C₅H₁₂ at -110 °C; ii, XC₆H₄SiMe₂F, -110 °C then to 20 °C; iii, Me₂SiHCl, -110 °C then to 20 °C; iv, I₂ in CCl₄ in presence of an excess of PhSiMe₃ for X = H, p-Cl, and m-CF₃ and of XC₆H₄SiMe₃ for X = p-OMe and p-Me.

as follows: (a) In the reactions with both alcohols there is a remarkably large spread of rates; the *p*-OMe is 1.9×10^5 times as reactive as the *m*-CF₃ compound in (CF₃)₂CHOH, and the corresponding factor in CF₃CH₂OH is 6.5×10^4 . The magnitudes of these substituent effects seem to leave no doubt that the aryl group must be nucleophilically involved in the rate-determining transition state, which can confidently be assumed to be formation of the intermediate [(2), R = Me] in an S_N1 process. (b) Values of log k_{rel} in both media gave excellent linear plots against σ -constants, with values of ρ of -7.77 (corr. coeff., 0.9994) and -6.68 (corr. coeff., 0.997), respectively.

Since the cation (2) closely resembles a Wheland-intermediate in an electrophilic aromatic substitution, and since the spread of rates is high, a correlation with σ^+ -constants, or with $[\sigma^+ r(\sigma^+ - \sigma)]$ with a value of r fairly close to unity, was expected. (Correlations with σ^+ , even for low values of ρ of 0.89 and 1.27, respectively, were found for solvolyses of the tosylates, $XC_6H_4CH_2CH_2O_3SC_6H_4Me$ -p in EtOH and CF₃CH₂OH, which involve anchimeric assistance by 1,2bridging).⁵ We very tentatively suggest that the origin of this anomaly may lie, at least in part, in the severe steric hindrance to solvation around the forming cationic centres on the route to the intermediate [(2), R = Me]. The transition state is presumably not far along the reaction co-ordinate towards [(2), R = Me] and there is little disturbance of the π -system of the aryl group, but because there is little dispersal of the charge by solvation a large part of it has to be taken up by the aromatic ring, and thus the substituent effects are abnormally large.

For comparison, the effects of the substituents were examined (under pseudo first-order conditions) for the $S_N 2$ displacement reaction of the iodides with KNCS in MeCN. Values of k_{rel} at 35 °C for a mixture of a solution of the iodide

(5—10 mg) in 50 µl of CCl₄ with 500 µl of 0.25 M KCNS in MeCN were as follows: X = p-OMe, 0.84; *p*-Me, 0.93; H, 1.00; *p*-Cl 1.4; *m*-CF₃, 1.93. A plot of log k_{rel} against σ^0 is reasonably linear (r = 0.996; $\rho = 0.55$). The substituent effects are consistent with normal through-bond transmission of electronic effects.

It is noteworthy that 1,3-aryl bridging is unknown for carbocations, whereas anchimeric assistance by more remote aryl groups, and, of course, by β -aryl groups, is well known.⁷

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