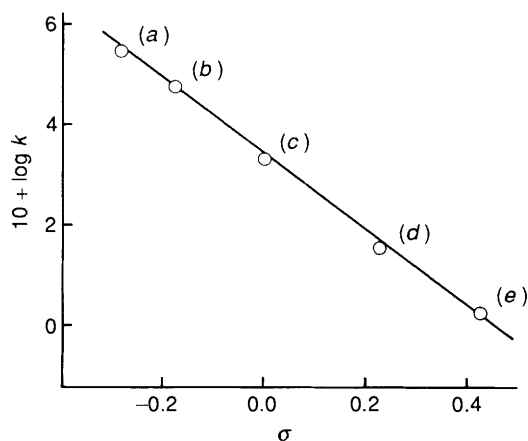


Table 1 Values of observed first-order rate constants, k , for reactions of the iodides **1** with fluorinated alcohols ROH at 35.0 °C

Y	$k/10^{-8} \text{ s}^{-1}$	
	R = (CF ₃) ₂ CH ₂	R = CF ₃ CH ₂
<i>p</i> -OMe	3.05×10^3	1.40×10^3
<i>p</i> -Me	6.3×10^2	1.65×10^2
H	2.02×10	1.75×10
<i>p</i> -Cl	3.7×10^{-1}	8.5×10^{-1}
<i>m</i> -CF ₃	1.6×10^{-2}	2.15×10^{-2}

**Fig. 1** Plot of $\log k$ against σ for reactions of the iodides **1** with (CF₃)₂CHOH. Numbering of points: (Y =) *p*-OMe, (a); *p*-Me, (b); H, (c); *p*-Cl, (d); *m*-CF₃, (e).

constants k are shown in Table 1. (The time, $t_{1/2}$, for half-completion of the reaction for Y = H was *ca.* 10 h.)

The most striking feature of the results is the very large spread of rates, involving a factor of 1.9×10^5 , between the iodides with Y = *p*-OMe and *m*-CF₃. The magnitude of the spread leaves no doubt that the aryl group is directly involved in the rate-determining step of the reaction, and the sequence of rate constants is consistent with the expected formation of the aryl-bridged intermediate **II** as the iodide leaves with the assistance of the electrophilic solvent.

Detailed analysis of the substituent effects, however, reveals an unexpected feature. Since the intermediate **II** is closely analogous to a Wheland intermediate (σ -complex) in a conventional electrophilic aromatic substitution the substituent effects would be expected to correlate with σ^+ -constants or possibly, in terms of the Yukawa–Tsuno equation, with the quantity $[\sigma + r(\sigma^+ - \sigma)]$ with r in the range *ca.* 0.7–1.2.⁷ In fact a plot of $\log k_{\text{rel}}$ against σ^+ is very far from linear, whereas a plot against the ordinary Hammett σ -constants is an excellent straight line (corr. coeff. = 0.999, Fig. 1). (Values of σ^- and σ^+ constants are taken from ref. 7). Furthermore the slope, ρ , has the very high value of -7.60 , higher, for example, than that of -6.2 for positive bromination of YC₆H₅ species (by HOBr–HClO₄ in 50% aqueous dioxane at 25 °C), though distinctly lower than that of -12.1 for molecular bromination (in CH₃CO₂H–H₂O at 25 °C).⁷ The high value in the solvolysis means that a substantial positive charge is developed on going to the transition state, and in a conventional electrophilic aromatic substitution this would normally be associated with a transition state well along the reaction coordinate towards the Wheland intermediate, and thus with a correlation with σ^+ or with $[\sigma + r(\sigma^+ - \sigma)]$ with a value of r in the region of unity; for example, for the positive bromination mentioned r is 1.15.⁷ The excellence of the correlation with σ in the solvolysis may be partly fortuitous, but we note that for a

correlation with σ^+ the rate constant for **1**, Y = *p*-OMe would have to be 6500 times as large as that observed in order to match the σ^+ -constant of -0.78 .

The correlation with σ could in principle arise from some special feature of **II** (*e.g.* a marked distortion of the geometry of the aryl group) and/or of the transition state on the way to it, that prevents effective conjugation between electron-releasing substituents and the developing positive charge, but we cannot realistically envisage any such feature and it is noteworthy that correlations with σ^+ (associated with low values of ρ of 0.89 and 1.27, respectively) were found for the solvolyses of the tosylates YC₆H₄CH₂CH₂O₃SC₆H₄Me-*p* in EtOH and CF₃CH₂OH, reactions which involve anchimeric assistance by 1,2-bridging.⁸ We suggest, as at least a partial explanation, that the high value of ρ is deceptive as an indication of the position of the transition state along the reaction coordinate on the way to **II**, perhaps because of very poor solvation of the forming cation, in which the positively-charged centres are effectively buried among methyl groups that inhibit approach of (CF₃)₂CHOH molecules, which in any case are very poor at providing the nucleophilic (as distinct from general electrostatic) solvation that is so important for carbocations. In the gas-phase the ρ factor for formation of the Wheland intermediate would be very much higher than that observed in solution, and a value of -17 has been estimated for protonation of substituted benzenes in the gas phase.^{9*} Thus the high value of ρ in the solvolysis might correspond to a fairly small movement along the reaction coordinate and so to a fairly small inherent charge development, but because there would be little dispersal of the charge by solvation there would be a much stronger than usual interaction with the substituents. Since the transition state would be not far removed from the initial state the substituents would influence the rates in accord with their σ^- rather than their σ^+ -constants.

The reaction with CF₃CH₂OH was studied at 25.0 °C in the same way, but with a 4/5 (v/v) mixture of CF₃CH₂OH–CDCl₃ containing two molar equivalents of Et₃N. Reactions were monitored to >85% completion except for **1**, Y = *m*-CF₃ which was taken to only 35% completion (in 31 weeks). Analyses by GLC–MS confirmed that the products were exclusively the expected trifluoroethoxides **2**, X = OCH₂CH₃. Again, good first-order kinetics were observed, and the values of k are shown in Table 1. (The values of the half-life, $t_{1/2}$, vary from 8.3 min for Y = *p*-OMe to almost a year for Y = *m*-CF₃.) The first feature of note is that the reactions are somewhat slower than those with (CF₃)₂CHOH even though the concentration of the latter was significantly lower, and this can be attributed to the less effective assistance by CF₃CH₂OH to the leaving of the iodide ion. In view of the lower reactivity of this alcohol the transition state would be expected to lie further along the reaction coordinate, resulting in a higher ρ value, whereas the equally good linear plot (corr. coeff. = 0.998) of $\log k_{\text{rel}}$ against σ has the slightly lower slope, ρ , of -6.56 . This can reasonably be attributed to the rather more effective solvation associated with the higher concentration, smaller bulk, and higher nucleophilic solvation ability of CF₃CH₂OH, which would mean that a smaller proportion of the developed charge would be available for interaction with the substituents.

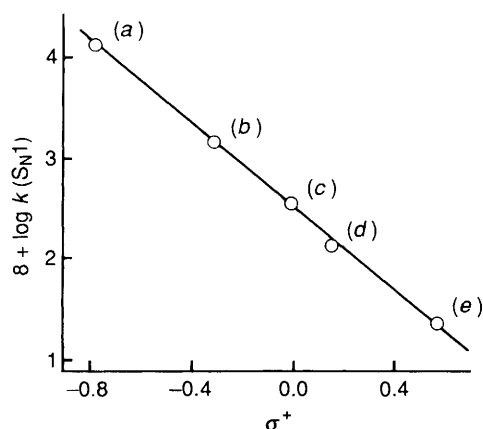
Reactions with MeOH.—The results obtained for the reactions with the fluorinated alcohols left no doubt that there is no participation by the external nucleophile in the rate-

* This value, which was estimated for the reaction at room temperature from the value of -22.8 derived from calculated data at 0 K, seems rather low in view of the value of -12.1 observed for molecular bromination (in which the charge on the ring will not be fully developed in the transition state) in the good solvating medium MeCO₂H–H₂O.⁷

Table 2 Observed first-order rate constants, k , for reactions of the iodides **1** with MeOH at 61.0 °C, and possible breakdowns into S_N1 and S_N2 components^a

Y	$k/10^{-8} \text{ s}^{-1}$	$r = 1.0$		$r = 0.5$	
		$k(S_N2)/10^{-8} \text{ s}^{-1}$	$k(S_N1)/10^{-8} \text{ s}^{-1}$	$k(S_N2)/10^{-8} \text{ s}^{-1}$	$k(S_N1)/10^{-8} \text{ s}^{-1}$
<i>p</i> -OMe	13 200	122	13 080	126	13 070
<i>p</i> -Me	1 550	134	1 416	140	1 410
H	510	145	365	150	360
<i>p</i> -Cl	340	218	122	225	115
<i>m</i> -CF ₃	300	280	20	290	10

^a Values of $k(S_N2)$ and $k(S_N1)$ under $r = 1$ are based on the value of $280 \times 10^{-8} \text{ s}^{-1}$ for $Y = m\text{-CF}_3$, selected to give a correlation with $[\sigma + (\sigma^+ - \sigma)]$. Those under $r = 0.5$ are based on the value of $290 \times 10^{-8} \text{ s}^{-1}$ for $Y = m\text{-CF}_3$, selected to give a correlation with $[\sigma + 0.5(\sigma^+ - \sigma)]$ (see text).

**Fig. 2** Plot of $\log k(S_N1)$ against σ^+ for reactions of iodides **1** with MeOH. Numbering of points as for Fig. 1.

determining step, *i.e.* that the reaction has an S_N1 mechanism. The results for the reaction with MeOH turned out to be more complex, and in a sense even more interesting.

Again a cosolvent was necessary, and a 15/50 (v/v) MeOH- CCl_4 mixture was used; the reaction was monitored in the usual way, and good first-order kinetics were observed up to the >80% extent of reaction studied. Analysis by GLC-MS at the end of the reaction revealed that within the limits of detection the products were exclusively the methoxides **2**, $X = \text{OMe}$ for $Y = p\text{-OMe}$ and $p\text{-Me}$, but for $Y = \text{H}$, $p\text{-Cl}$, and $m\text{-CF}_3$ *ca.* 10, 15 and 20%, respectively, of the hydroxide **2**, $X = \text{OH}$ was formed along with the methoxide, revealing that our MeOH, although dried by a standard method, contained some water.

From the values of k shown in Table 2 it will be seen that, as expected in view of the much lower electrophilicity of methanol, the reactions were much slower than those with the fluorinated alcohols, and a temperature of 61.0 °C was used. The most striking feature of the results in comparison with those for the reactions with the fluorinated alcohols is the very small spread of rates, the factor between the *p*-OMe and *m*-CF₃ compounds being only 44. Furthermore it is apparent that there is a fairly large, 26-fold, fall in rate on going from the *p*-OMe to the unsubstituted compound, then only a 1.7-fold fall on going to the *m*-CF₃ derivative. It follows that a plot of $\log k$ against either σ or σ^+ is far from linear.

We suggest that the smallness of the rate change on going from the parent compound to the *p*-Cl and *m*-CF₃ compounds provides the clue to what is happening, namely that for these compounds there is substantial contribution from a bimolecular, S_N2 , mechanism involving direct attack of the nucleophiles MeOH and H_2O on the Si-I bond, the mechanism believed to operate in the methanolysis of $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{I}$.¹⁰ However, for the iodides **1** this is not the only mechanism operating, since if it were the rates would rise on going from

($Y =$) H to *p*-Cl to *m*-CF₃. (See the later discussion of the hydrolysis and the reactions with KSCN in MeCN.) The pattern of values of k can be accounted for on the basis of the assumption that for all the aryl compounds there are two competing mechanisms operating, the S_N1 and S_N2 processes, with the S_N1 generally dominating for the *p*-OMe compounds and the S_N2 for the *m*-CF₃ compounds.

It is possible to interpret (or perhaps, more strictly, to simulate) the pattern of substituent effects in quantitative terms by making the assumptions that (a) the value of k for the *m*-CF₃ compound refers almost completely to the S_N2 process, and (b) the rate constants $k(S_N2)$, for the S_N2 process fall progressively on going from the *m*-CF₃ to the *p*-OMe compound in much the same way as they do in the S_N2 reaction with KSCN in MeCN, described later. Thus if of the observed rate constant, k , of $3.00 \times 10^{-6} \text{ s}^{-1}$ for the compound with $Y = m\text{-CF}_3$ a value of $2.80 \times 10^{-6} \text{ s}^{-1}$ is assigned to the contribution, $k(S_N2)$, by the S_N2 component, then the values of $k(S_N1)$ for the other compounds, calculated on the basis of assumption (b), are those shown in Table 2 for $r = 1$. The contributions, $k(S_N1)$, from the S_N1 components are then as shown in Table 2, and values of $\log k(S_N1)$ correlate well with σ^+ -constants (corr. coeff., 0.999; ρ , -2.10), as can be seen from Fig. 2. But if a value of $2.90 \times 10^{-6} \text{ s}^{-1}$ is assigned to $k(S_N2)$ for the *m*-CF₃ compound, the consequent values of $k(S_N1)$ show an almost equally good correlation (corr. coeff., 0.999; ρ , -2.98) with $[\sigma + r(\sigma^+ - \sigma)]$ where $r = 0.5$. However, no realistic values of $k(S_N2)$ can be chosen to lead to a satisfactory correlation with σ .

In terms of this interpretation, even for the parent compound with $Y = \text{H}$ the S_N2 process makes a contribution of *ca.* 30% to the overall observed rate constant. The more complex nature of the results for the reactions with MeOH compared with those for the reactions with the fluorinated alcohols arises from the fact that the S_N1 processes are much faster in those alcohols because they are much more effective at providing electrophilic assistance to the leaving of the iodide ion, whereas the S_N2 processes are much faster in MeOH because of its much higher nucleophilicity. Because of its smaller size, water is much more effective as a nucleophile towards these highly crowded systems and so for operation of the S_N2 mechanism even a trace of water can bring about a significant proportion of hydrolysis. (The presence of *ca.* 0.01% of water in the methanol could give rise to the observed 20% yield of hydroxide from **1**, $Y = m\text{-CF}_3$.) In contrast the highly reactive and less sterically hindered intermediate selects much less effectively between MeOH and H_2O , so that little hydroxide is formed when the S_N1 processes are greatly dominant, *i.e.* for the *p*-OMe and *p*-Me compounds.

It is not possible to make a satisfactory analysis of the data if $\log k(S_N1)$ is assumed to be linearly related to σ , as it is for the reactions in the fluorinated alcohols. As noted earlier, some σ^+ -contribution to the substituent effects would normally be expected for a rate-determining step involving formation of the

Table 3 Observed first-order rate constants, k , for reactions of the iodides **1** with H_2O at 61.0°C , and possible breakdown into $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ components^a

Y	$k/10^{-8} \text{ s}^{-1}$	$k(\text{S}_{\text{N}}2)/10^{-8} \text{ s}^{-1}$	$k(\text{S}_{\text{N}}1)/10^{-8} \text{ s}^{-1}$
<i>p</i> -OMe	8050	1600	6450
<i>p</i> -Me	2300	1750	550
H	2300	2120	180
<i>p</i> -Cl	2870	2790	80
<i>m</i> -CF ₃	3050	3035	15

^a Values of $k(\text{S}_{\text{N}}2)$ are selected from within reasonable limits to give a linear plot of $\log k(\text{S}_{\text{N}}1)$ against σ^+ (see text).

Table 4 First-order rate constants, k , for reactions of the iodides **1** (ca. $0.02\text{--}0.04 \text{ mol dm}^{-3}$) with ca. 0.23 mol dm^{-3} KSCN in MeCN- CCl_4 at 35.0°C ^a

Y	$k/10^{-5} \text{ s}^{-1}$
<i>p</i> -OMe	7.7
<i>p</i> -Me	8.55
H	9.2
<i>p</i> -Cl	12.8
<i>m</i> -CF ₃	17.8

^a The medium comprised 500 mm^3 of 0.25 mol dm^{-3} KSCN (in MeCN) and 50 mm^3 of CCl_4 .

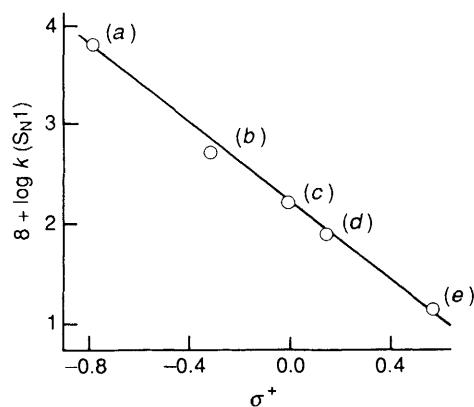


Fig. 3 Plot of $\log k(\text{S}_{\text{N}}1)$ against σ^+ for hydrolysis of the iodides. Numbering of points as for Fig. 1.

intermediate **II**, and it is the absence of such a contribution in the fluorinated media that is surprising not its presence in the methanolysis. Other things being equal, the transition state in the formation of the intermediate **II** would be expected to be further along the reaction coordinate for the reaction in MeOH because of the poorer electrophilic assistance to the leaving of the iodide ion, and so there should be a greater demand on the conjugative electron-releasing effects of substituents, showing up in the need to use σ^+ -constants or the Yukawa-Tsuno equation with a value of r of 0.5 or more. The fact that the value of ρ is much smaller than in the reactions with the fluorinated alcohols, in spite of the suggested location of the transition state closer to the intermediate **II**, can be attributed to the more effective solvation of the forming cation by MeOH.

We note finally that $t_{\frac{1}{2}}$ at 61°C for the $\text{S}_{\text{N}}2$ reaction of **1**, $\text{Y} = \text{H}$ with MeOH (diluted with CDCl_3) derived from the estimated value of $k(\text{S}_{\text{N}}2)$ in Table 2 is 5.6 days, reasonably consistent with the ca. 13 days observed for methanolyses of $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{I}$ at 50°C in neat MeOH,¹¹ a reaction now believed to be of the $\text{S}_{\text{N}}2$ type.¹⁰ It is of interest that the vinyl-containing iodide $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)(\text{SiMe}_2\text{I})$ is only slightly more reactive towards MeOH than $\text{TsiSiMe}_2\text{I}$, implying that there is also no $\text{S}_{\text{N}}1$ component in the case of

the former iodide, and thus that anchimeric assistance by the vinyl group is significantly weaker than that by the phenyl group.

Hydrolysis.—For the studies of the reactions with water a solution of the iodide (5–10 mg) in CCl_4 (50 mm^3) was placed in an NMR tube and 530 mm^3 of a 5 vol% solution of water in dioxane was added. The reactions were carried out at 61.0°C and monitored in the usual way to $>70\%$ completion. The products were shown from their ^1H NMR and mass spectra to be exclusively the expected hydroxides. Good first-order kinetics were observed and the values of the observed first-order rate constants, k , are shown in Table 3.

The striking features of the results are the very small overall spread of rates and the fact that the rate falls by a factor of 3.5 on going from the *p*-OMe to the *p*-Me compound, stays constant on going to the parent compound, then rises slightly but significantly on going to the *p*-Cl and *m*-CF₃ compounds. It is immediately obvious that the compounds with $\text{Y} = \text{H}$, *p*-Cl, and *m*-CF₃ cannot be reacting to any great extent by the $\text{S}_{\text{N}}1$ mechanism since electron-withdrawal raises the rate. It seems that, as in the methanolyses, the $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ processes operate together, with the $\text{S}_{\text{N}}1$ clearly predominating for $\text{Y} = \text{p-OMe}$ and the $\text{S}_{\text{N}}2$ predominating for $\text{Y} = \text{p-Me}$, and greatly so for $\text{Y} = \text{H}$, *p*-Cl, and *m*-CF₃.

In principle the type of approach used for the analysis of the data for methanolysis can be used in this case also. Again the observed pattern of rate constants can be simulated, but with less certainty because the estimated values of the rate constants $k(\text{S}_{\text{N}}1)$ for the compounds with $\text{Y} = \text{H}$, *p*-Cl, and *m*-CF₃ are so small that they are comparable with (or for $\text{Y} = \text{m-CF}_3$ well within) the experimental uncertainty in the total observed rate constant. Nevertheless, if it is assumed that the substituent effects in the $\text{S}_{\text{N}}1$ process can be correlated in terms of the Yukawa-Tsuno equation with $[\sigma + r(\sigma^+ - \sigma)]$ with $r = 1.0$ then a reasonable simulation of the results can be obtained on the basis of the suggested values of $k(\text{S}_{\text{N}}1)$ and $k(\text{S}_{\text{N}}2)$ shown in Table 3. The values of $k(\text{S}_{\text{N}}2)$ are chosen arbitrarily but from within reasonable limits to produce the good linear plot (corr. coeff., 0.995, ρ , -2.10) of $\log k(\text{S}_{\text{N}}1)$ against σ^+ shown in Fig. 3. A markedly less satisfactory plot can be obtained by use of an r value of 0.5 in association with other reasonable, appropriately-selected, values of $k(\text{S}_{\text{N}}2)$ for the *p*-Cl and *m*-CF₃ compounds, but no reasonable choice of $k(\text{S}_{\text{N}}2)$ values can produce even a very roughly linear plot of $\log k(\text{S}_{\text{N}}1)$ against σ .

It would be possible in principle to determine the correct value of r for the hydrolysis by using substituents more electron-releasing than *p*-OMe, or suitable combinations of two substituents in the aryl ring, but the necessary syntheses would be tiresome.

For comparison the hydrolysis of $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{I}$ was examined under the same conditions. A first order rate constant of $6.7 \times 10^{-6} \text{ s}^{-1}$ ($t_{\frac{1}{2}} = 28.6 \text{ h}$) was observed, smaller by a factor of ca. 3.1 than the value estimated for the $\text{S}_{\text{N}}2$ component for **1**, $\text{Y} = \text{H}$. This factor is similar to that estimated above for the methanolysis. It is noteworthy that the very similar reactivity factor of 3.2 was observed between **1**, $\text{Y} = \text{H}$ and $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{I}$ in the $\text{S}_{\text{N}}2$ reaction with KSCN at 61°C , providing support for the validity of the assessments of the $\text{S}_{\text{N}}2$ contributions in the methanolysis and hydrolysis of compounds **1**. We note also that in the $\text{S}_{\text{N}}1$ process ca. 50% of the product should have the aryl group on the α -Si rather than in its original position on the γ -Si, and the proportion of rearrangement observed in the hydrolysis of the closely related iodide $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Ph})(\text{SiEt}_2\text{I})$ ¹² is consistent with the estimated ratio of the $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ contributions in the hydrolysis of **1**, $\text{Y} = \text{H}$.

Reactions with KSCN in MeCN.—In order to provide a guide to the substituent effects in an unambiguously S_N2 reaction of compounds **1** the reaction with a large excess of KSCN in MeCN was examined. About 5–10 mg of the iodide were dissolved in 50 mm³ of CCl₄ in an NMR tube and 500 mm³ of an 0.25 mol dm⁻³ solution of KSCN in anhydrous MeCN was added. The reaction, at 35 °C, was monitored in the usual way (to 65% completion for Y = *p*-OMe and >78% for the other compounds) and (under the pseudo-first-order conditions) good first-order kinetics were observed. The products were shown to be exclusively the expected isothiocyanates **2**, Y = NCS. The values of the observed first order rate constant *k* are shown in Table 4. As expected for a reaction involving direct attack of a nucleophile on the silicon of the Si–I bond, electron-withdrawing substituents increase and electron-releasing substituents lower the rate. The effects correlate satisfactorily with σ° -constants¹³ (corr. coeff., 0.999; ρ , 0.62), in keeping with the view that the substituents exert their influence by transmission of the electronic effects through the bonding system –Si–C–Si. A similar correlation was previously observed for the corresponding reactions of the related iodides (Me₃Si)₃CSiH(C₆H₄Y)I, though the ρ -value (2.1) was higher in that case, as expected since the aryl group was attached directly to the functional silicon centre.¹⁰ As noted earlier, the rate constant determined for the reaction of (Me₃Si)₃CSiMe₂I with KSCN under the conditions used for the reactions of iodides **1**, viz. $2.9 \times 10^{-5} \text{ s}^{-1}$, was smaller than that for **1**, Y = H by a factor of 3.2. This is consistent with the increase in electron withdrawal from the reaction centre on replacement of an Me by a Ph group.

Conclusions

The results seem to leave no doubt that the aryl groups in the iodides **1** can provide powerful anchimeric assistance to the leaving of the iodide ion and so promote solvolysis by the S_N1 mechanism. The assistance can be confidently associated with rate-determining formation of the aryl-bridged intermediates **II**. In the reactions with fluorinated alcohols (CF₃)₂CHOH and CF₃CH₂OH this is the sole solvolysis mechanism, but in those with MeOH and H₂O an S_N2 mechanism also operates, and is greatly dominant for **1**, Y = *p*-Cl or *m*-CF₃. The patterns of the effects of the substituents Y in the S_N1 components of the methanolysis and hydrolysis seem to be reasonably normal for a process analogous to that of a conventional electrophilic aromatic substitution. Those in the reactions with fluorinated alcohols appear somewhat anomalous in showing excellent correlation with σ -constants, though steric hindrance to solvation of the forming cation **I** in these very congested systems may provide at least a partial explanation. It is noteworthy that 1,3-aryl bridging of the type shown in **I** is unknown for bridging between carbon centres in carbocations, whereas anchimeric assistance by more remote aryl groups, and, of course, β -aryl groups, is well known.¹⁴

Experimental

Materials.—The preparations of the iodides and some related compounds will be described elsewhere.⁶ Methanol was dried by distillation from Mg(OMe)₂ and stored over 3 Å molecular sieve. Acetonitrile was distilled from P₂O₅ and stored over 4 Å molecular sieve. Hexafluoroisopropanol trifluoroethanol, and deuteriochloroform were refluxed over, and distilled from, CaH₂ and stored over 4 Å molecular sieve. Tetra- and dichloromethane were refluxed over CaCl₂, distilled off, and stored over 4 Å molecular sieve. Potassium thiocyanate, of analytical reagent grade, was dried at 100 °C under a pressure of 0.1 Torr.

Instrumentation.—The ¹H NMR spectra were recorded at 90 MHz on a Perkin-Elmer R32 spectrometer. Mass spectra (EI at 70 eV) were obtained with a Kratos MS-25 spectrometer. For linked GLC–MS a packing of 5% OV-101 or 3% OV-17 on GasChrom G was used.

Reactions with Hexafluoroisopropanol.—A sample (5–10 mg) was placed in an NMR tube and dissolved in CDCl₃ (600 mm³) containing two equivalents of Et₃N. The (CF₃)₂CHOH (200 mm³) was added and the tube quickly sealed, shaken briefly, and then kept at 35.0 °C either in the probe of the spectrometer (Y = *p*-OMe, *p*-Me) or in a thermostatically-controlled water bath. The NMR spectra were recorded at intervals and the heights (*h* and *h'*, respectively) of the signals from the Me₃Si groups in the starting material and product were measured. A plot of log [*h*/(*h* + *h'*)] against time then gave the first-order rate constant. There was no significant departure from first-order behaviour for the extents of reaction monitored, viz. 70–75% for Y = *p*-OMe, *p*-Me and H, 55% for Y = *p*-Cl, and 17% for Y = *m*-CF₃. The rate constants are shown in Table 1.

The reactions were taken to completion at 35 °C for Y = *p*-OMe, and H, and at 60 °C for Y = *p*-Cl and *m*-CF₃. The solvents were then evaporated off, the residue taken up in CCl₄ containing 5% of CH₂Cl₂, and the ¹H NMR spectrum recorded. The solution was then subjected to analysis by GLC–MS, which revealed the presence only of the hydroxide in each case. The ¹H and mass spectral data were essentially identical to those of the products obtained from the hydrolysis in H₂O–dioxane, described later. For Y = *m*-CF₃, the reaction solution after 136 days was evaporated and the residue taken up as usual in CCl₄ containing 5% CH₂Cl₂. The ¹H NMR spectrum and analysis by linked GLC–MS showed that it consisted of a ca. 4:1 mixture of the starting material and the hydroxide.

Reactions with 2,2,2-Trifluoroethanol.—The procedure was identical to that described above except that 400 mm³ of CDCl₃ (containing two molar equivalents of Et₃N) and 500 mm³ of CF₃CH₂OH were used. The reactions were monitored to >80% completion except for that for Y = *m*-CF₃, which was taken to only 35% completion. The products were identified as before; relevant ¹H NMR and mass spectral data are given below:

Y = *p*-OMe: δ 0.15 (s, 6 H, SiMe₂OCH₂F₃), 0.23 (s, 18 H, SiMe₃), 0.53 (s, 6 H, SiMe₂ aryl), 3.78 (s, 3 H, OMe), 3.89 (q, 2 H, CH₂CF₃), 6.69–7.80 (m, 4 H, C₆H₄); *m/z* 465 (80%, [M – Me]⁺), 365 (20), 205 (25), 165 (60, SiMe₂C₆H₄OMe) 73 (100).

Y = *p*-Me: δ 0.16 (s, 6 H, SiMe₂OCH₂CF₃), 0.23 (s, 18 H, SiMe₃), 0.54 (s, 6 H, SiMe₂ aryl), 2.32 (s, 3 H, *p*-Me), 3.85 (q, 2 H, J 8.50, SiOCH₂CF₃), 6.97–7.67 (m, 4 H, C₆H₄); *m/z* 449 (25%, [M – Me]⁺), 349 (5), 261 (10), 205 (30), 149 (80, SiMe₂C₆H₄Me), 73 (100).

Y = H: δ 0.14 (s, 6 H, SiMe₂OCH₂CF₃), 0.24 (s, 18 H, SiMe₃), 0.57 (s, 6 H, SiMe₂Ph), 3.85 (q, 2 H, J 8.50, SiOCH₂CF₃), 7.17–7.87 (m, 5 H, Ph); *m/z* 435 (100%, M – Me⁺), 355 (20), 335 (25), 300 (10), 247 (15), 205 (40), 175 (25), 135 (50, SiMe₂Ph), 73 (40).

Y = *p*-Cl: δ 0.16 (s, 6 H, SiMe₂OCH₂CF₃), 0.24 (s, 18 H, SiMe₃), 0.54 (s, 6 H, (SiMe₂ aryl), 3.86 (q, 2 H, J 9.0, SiOCH₂CF₃), 7.18–7.76 (m, 4 H, C₆H₄); *m/z* 469 (100%, [M – Me]⁺), 369 (20), 281 (10), 205 (35), 169 (20, SiMe₂C₆H₄Cl), 73 (50).

Y = *m*-CF₃: δ 0.14 (s, 6 H, SiMe₂OCH₂CF₃), 0.25 (s, 18 H, SiMe₃), 0.60 (s, 6 H, SiMe₂ aryl), 3.86 (q, 2 H, J 9.0, SiOCH₂CF₃), 7.36–8.16 (m, 4 H, C₆H₄); *m/z* 503 (100%, [M – Me]⁺), 423 (30), 203 (20, SiMe₂C₆H₄CF₃), 73 (40).

Reactions with Methanol.—The iodide (5–10 mg) was

dissolved in CCl_4 (150 mm^3) in an NMR tube and methanol (500 mm^3) was added. The subsequent procedure was as described above except that the tubes were kept at 61.0 °C in a water bath. Good first-order kinetics were observed for the extents of reaction monitored (>80%), and the rate constants are shown in Table 1. Rate constants were reproducible to within $\pm 5\%$.

Reactions were taken to completion and the products examined as described above. In the case of the compounds with $Y = p\text{-OMe}$ and $p\text{-Me}$, the ^1H NMR spectra and analysis by GLC-MS revealed the presence only of the corresponding methoxides. For $Y = \text{H}$, $p\text{-Cl}$, and $m\text{-CF}_3$, although only the signals from the methoxides were observed in the NMR spectrum, the analysis by GLC-MS showed that in the other cases some of the hydroxide was present, specifically for ($Y =$) H , 10; $p\text{-Cl}$, 15; and $m\text{-CF}_3$, 20%. The ^1H NMR and mass spectral data for the methoxides were as follows:

$Y = p\text{-OMe}$: δ 0.11 (s, 6 H, SiMe_2), 0.20 (s, 18 H, SiMe_3), 0.49 (s, 6 H, SiMe_2 aryl), 3.41 (s, 3 H, SiOMe), 3.78 (s, 3 H, $p\text{-OMe}$), 6.67–7.69 (m, 4 H, C_6H_4); m/z 397 (100%, $[\text{M} - \text{Me}]^+$), 365 (15), 305 (10), 277 (10), 217 (25), 201 (10), 187 (10), 165 (35, $\text{SiMe}_2\text{C}_6\text{H}_4\text{OMe}$), 73 (20).

$Y = p\text{-Me}$: δ 0.10 (s, 6 H, SiMe_2O), 0.19 (s, 18 H, SiMe_3), 0.49 (s, 6 H, SiMe_2 aryl), 2.32 (s, 3 H, $p\text{-Me}$), 3.40 (s, 3 H, OMe), 6.96–7.66 (m, 4 H, C_6H_4); m/z 381 (100%, $[\text{M} - \text{Me}]^+$), 349 (15), 315 (10), 261 (10), 217 (10), 149 (15, $\text{SiMe}_2\text{C}_6\text{H}_4\text{Me}$), 73 (30).

$Y = \text{H}$: δ 0.09 (s, 6 H, SiMe_2O), 0.19 (s, 18 H, SiMe_3), 0.52 (s, 6 H, SiMe_2Ph), 3.39 (s, 6 H, OMe), 7.13–7.84 (m, 5 H, Ph); m/z 367 (80%, $[\text{M} - \text{Me}]^+$), 279 (15), 275 (10), 263 (10), 247 (25), 217 (30), 201 (20), 187 (20), 175 (25), 135 (50, SiMe_2Ph), 129 (15), 121 (10), 89 (15), 73 (100), 59 (30).

$Y = p\text{-Cl}$: δ 0.11 (s, 6 H, SiMe_2O), 0.20 (s, 18 H, SiMe_3), 0.49 (s, 6 H, SiMe_2 aryl), 3.41 (s, 3 H, OMe), 7.15–7.76 (m, 4 H, C_6H_4); m/z 401 (85, $[\text{M} - \text{Me}]^+$), 369 (15), 281 (10), 217 (15), 169 (15, $\text{SiMe}_2\text{C}_6\text{H}_4\text{Cl}$), 89 (20), 73 (100), 59 (35, SiMe_2H).

$Y = m\text{-CF}_3$: δ 0.11 (s, 6 H, SiMe_2O), 0.21 (s, 18 H, SiMe_3), 0.56 (s, 6 H, SiMe_2 aryl), 3.43 (s, 3 H, OMe), 7.27–8.28 (m, 4 H, C_6H_4); m/z 435 (100%, $[\text{M} - \text{Me}]^+$), 404 (15), 73 (20).

The mass spectral data for the hydroxides were essentially the same as those of samples obtained from hydrolysis in H_2O -dioxane (see below).

Reactions with Water.—The procedure was as described for the methanolysis except that the medium was made up of CCl_4 (50 mm^3) and a mixture of 5.48 vol% H_2O -dioxane (530 mm^3). Reactions were monitored to >75% completion and good first-order plots were obtained. The rate constants are shown in Table 3. Values were reproducible to within $\pm 5\%$. The rate constant determined for $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{I}$ under identical conditions was $3.05 \times 10^{-5} \text{ s}^{-1}$.

Reactions were taken to completion and the usual work-up and analysis showed the product in each case to be exclusively the expected hydroxide. Relevant ^1H NMR and mass spectral data were as follows:

$Y = p\text{-OMe}$: δ 0.19 (s, 6 H, SiMe_2O), 0.21 (s, 18 H, SiMe_3), 0.53 (s, 6 H, SiMe_2 aryl), 1.26 (br s, 1 H, OH), 3.78 (s, 3 H, $p\text{-OMe}$), 6.69–7.80 (m, 4 H, C_6H_4); m/z 398 (5%, M^+), 383 (55, $\text{M} - \text{Me}$), 367 (20, $\text{M} - \text{MeH} - \text{Me}$), 290 (10), 275 (100, $\text{M} - \text{C}_6\text{H}_4\text{OMe} - \text{Me}$), 187 (15), 165 (20), 73 (15).

$Y = p\text{-Me}$: δ 0.19 (s, 6 H, SiMe_2O), 0.21 (s, 18 H, SiMe_3), 0.54 (s, 6 H, SiMe_2 aryl), 1.26 (br s, 1 H, OH), 2.33 (s, 3 H, $p\text{-Me}$), 6.95–7.75 (m, 4 H, C_6H_4); m/z 367 (95%, $[\text{M} - \text{Me}]^+$), 351 (40), 275 (100, $\text{M} - \text{C}_6\text{H}_5\text{Me} - \text{Me}$), 187 (25), 149 (40), 73 (55).

$Y = \text{H}$: δ 0.20 (s, 6 H, SiMe_2O), 0.22 (s, 18 H, SiMe_3), 0.57 (s, 6 H, SiMe_2Ph), 1.41 (br s, 1 H, OH), 7.16–7.89 (m, 5 H, C_6H_5); m/z 353 (85%, $[\text{M} - \text{Me}]^+$), 337 (85, $\text{M} - \text{MeH} -$

Me), 323 (10), 275 (100, $\text{M} - \text{Me} - \text{Ph}$), 265 (10), 247 (15), 215 (15), 203 (35), 187 (55), 175 (20), 135 (65), 73 (50).

$Y = p\text{-Cl}$: δ 0.22 (s, 24 H, $\text{SiMe}_2\text{O} + \text{SiMe}_3$), 0.54 (s, 6 H, SiMe_2 aryl), 1.26 (br s, 1 H, OH), 7.20–7.87 (m, 4 H, C_6H_4); m/z 387 (100%, $[\text{M} - \text{Me}]^+$), 371 (40, $\text{M} - \text{MeH} - \text{Me}$), 275 (40), 203 (15), 187 (20), 169 (15), 73 (50).

$Y = m\text{-CF}_3$: δ 0.19 (s, 6 H, SiMe_2O), 0.22 (s, 18 H, SiMe_3), 0.60 (s, 6 H, SiMe_2 aryl), 1.42 (br s, 1 H, OH), 7.17–8.27 (m, 4 H, C_6H_4); m/z 421 (55%, $[\text{M} - \text{Me}]^+$), 203 (20), 73 (100), 59 (10).

Reactions with KSCN in MeCN.—The iodide (5–10 mg) was dissolved in CCl_4 (50 mm^3), a 0.25 mol dm^{-3} solution of KSCN in MeCN (500 mm^3) was added and the tube was capped, shaken briefly, and kept at 35.0 °C in a thermostatically-controlled water bath. The progress of the reaction was monitored in the usual way, but for $Y = p\text{-Cl}$ the peak for the protons of the SiMe_2NCS group in the product coincided with that for the protons of the Me_3Si groups in the iodide, and an appropriate correction had to be made. Good first-order kinetics were observed for the extent of reaction monitored (>80%), and the rate constants are shown in Table 4. They were reproducible to within $\pm 5\%$. A rate constant of $2.86 \times 10^{-5} \text{ s}^{-1}$ was obtained for $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{I}$ under the same conditions.

Reactions were taken to completion and the solvent was then evaporated off and the residue was extracted with CCl_4 containing 5% of CH_2Cl_2 . The ^1H NMR spectrum of the solution was recorded, and the solution then subjected to GLC-MS. In all cases only the expected isothiocyanate was detected. The ^1H NMR and mass spectral data for the products were as follows:

$Y = p\text{-OMe}$: δ 0.29 (s, 18 H, SiMe_3), 0.32 (s, 6 H, SiMe_2NCS), 0.58 (s, 6 H, SiMe_2 aryl), 3.81 (s, 3 H, OMe), 6.74–7.72 (m, 4 H, C_6H_4); m/z 439 (30%, M^+), 424 (50, $\text{M} - \text{Me}$), 365 (40), 259 (15), 244 (10), 201 (15), 165 (100, $\text{SiMe}_2\text{C}_6\text{H}_4\text{OMe}$), 135 (10), 73 (45).

$Y = p\text{-Me}$: δ 0.29 (s, 18 H, SiMe_3), 0.33 (s, 6 H, SiMe_2NCS), 0.59 (s, 6 H, SiMe_2 aryl), 2.34 (s, 3 H, $p\text{-Me}$), 7.04–7.74 (m, 4 H, C_6H_4); m/z 423 (15%, M^+), 408 (70, $\text{M} - \text{Me}$), 349 (85, $\text{M} - \text{Me}_3\text{SiH}$), 277 (10), 261 (30), 259 (20), 244 (20), 216 (10), 201 (30), 189 (20), 149 (100, $\text{SiMe}_2\text{C}_6\text{H}_4\text{Me}$), 73 (90).

$Y = \text{H}$: δ 0.30 (s, 18 H, SiMe_3), 0.32 (s, 6 H, SiMe_2NCS), 0.62 (s, 6 H, SiMe_2Ph), 7.20–7.86 (m, 5 H, Ph); m/z 409 (10%, M^+), 394 (100, $\text{M} - \text{Me}$), 335 (85, $\text{M} - \text{Me}_3\text{SiH}$), 259 (15), 247 (15), 201 (20), 175 (15), 135 (30), 73 (60).

$Y = p\text{-Cl}$: δ 0.29 (s, 18 H, SiMe_3), 0.33 (s, 6 H, SiMe_2NCS), 0.61 (s, 6 H, SiMe_2 aryl), 7.22–7.78 (m, 4 H, C_6H_4); m/z 443 (5%, M^+), 428 (85, $\text{M} - \text{Me}$), 368 (40), 259 (10), 244 (10), 201 (15), 169 (25), 73 (100), 59 (15).

$Y = m\text{-CF}_3$: δ 0.30 (s, 18 H, SiMe_3), 0.32 (s, 6 H, SiMe_2NCS), 0.66 (s, 6 H, SiMe_2 aryl), 7.36–8.07 (m, 6 H, C_6H_4); m/z 462 (70%, $[\text{M} - \text{Me}]^+$), 403 (35, $\text{M} - \text{Me}_3\text{SiH}$), 315 (15), 244 (10), 203 (30, $\text{SiMe}_2\text{C}_6\text{H}_4\text{CF}_3$), 73 (100), 59 (10).

Isolation of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Ph})(\text{SiMe}_2\text{OH})$.—(a) The iodide (**I**, $Y = \text{H}$) (0.10 g) was dissolved in a few drops of CCl_4 and 2 vol% H_2O -MeCN (20 cm^3) was added. The mixture was kept at 60 °C for 3 days and then evaporated to dryness. The residue was sublimed under reduced pressure to give (*hydroxydimethylsilyl*)[*dimethyl(phenyl)silyl*]*bis(trimethylsilyl)methane* (0.054 g, 70%), m.p. 66 °C (Found: C, 55.3; H, 10.1. $\text{C}_{17}\text{H}_{36}\text{O}_4\text{Si}$ requires: C, 55.4; H, 9.85%). The ^1H NMR and mass spectral data were as given above.

(b) A similar procedure was carried out but with 2 vol% H_2O - Me_2SO in place of H_2O -dioxane and with reaction for only 20 h at 60 °C. The Me_2SO was removed by adding CCl_4 and shaking the solution several times with water. The organic layer was finally separated, dried (MgSO_4), filtered, and evaporated to dryness under reduced pressure. Sublimation

under reduced pressure then gave the hydroxide (69%) with properties as described under (a).

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