# Proportion of 1,3-Phenyl Migration in Trifluoroethanolysis, Methanolysis, and Hydrolysis of $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2I)$

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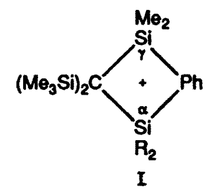
Solvolysis of the iodide $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2I)$, **2**, in $CF_3CH_2OH–CCl_4$ has been shown to give the rearranged and unrearranged products, $(Me_3Si)_2C(SiEt_2Ph)(SiMe_2OCH_2CF_3)$ and $(Me_2Si)_2C(SiMe_2Ph)(SiEt_2OCH_2CF_3)$, respectively, in *ca.* 85:15 ratio. Reaction of **2** with $MeOH–CCl_4$ gives the rearranged and unrearranged methoxides in *ca.* 75:25 ratio in the presence of $Ag_2SO_4$ (which promotes the formation of a Ph-bridged cation) and *ca.* 65:35 in its absence. In contrast, reaction with water–dioxane gives the rearranged and unrearranged hydroxides in only *ca.* 20:80 ratio, but the ratio becomes *ca.* 60:40 if $Ag_2SO_4$ is present. The results provide confirmation of the view reached previously, on the basis of the effects of the substituents Y on the rates of solvolyses of the compounds $(Me_3Si)_2C(SiMe_2C_6H_4Y)(SiMe_2I)$, that the parent compound (Y = H) undergoes trifluoroethanolysis exclusively by an $S_N1$ process (involving rate-determining formation of a phenyl-bridged cation), hydrolysis very predominantly by an $S_N2$ process but with a small $S_N1$ contribution, and methanolysis by a mixture of $S_N1$ and $S_N2$ processes with the former slightly predominating.

We recently concluded from analysis of the effects of the substituents Y on the rates of solvolysis of the iodides $(Me_3Si)_2C(SiMe_2C_6H_4Y)(SiMe_2I)$ that the reaction can proceed by either an $S_N1$ or an $S_N2$ process or a mixture of both, the relative contributions of the two processes varying with Y and the nature of the solvent.[1] Thus in the case of the parent compound, **1**, we judged that in the weakly nucleophilic but moderately electrophilic alcohols $(CF_3)_2CHOH$ and $CF_3CH_2OH$ (both containing $CDCl_3$) reaction takes place exclusively by the $S_N1$ process, involving rate-determining formation of the intermediate cation **I**, R = Me, which is then attacked by the solvent at either the α- or γ-Si centre. In contrast the hydrolysis of **1** in dioxane was judged to take place very predominantly by the $S_N2$ process, involving direct nucleophilic displacement of iodide ion by water, with only *ca.* 10% of the reaction following the $S_N1$ route. Between these two extremes, the reaction with MeOH (containing some $CCl_4$) was judged to proceed to the extent of *ca.* 70% by the $S_N1$ route and *ca.* 30% by the $S_N2$ route.[1]

**$(Me_3Si)_2C(SiMe_2Ph)(SiR_2I)$**

**1** R = Me
**2** R = Et



**I**

In the case of the iodide $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2I)$, **2**, reaction by the $S_N1$ route would be expected to give some rearranged product as a result of nucleophilic attack of the solvent, MOH, at the γ-Si centre in the intermediate **I**, R = Et (*cf.* ref. 2), and attack at the γ-Si should be somewhat easier than at the α-Si because of the greater steric hindrance at the latter centre, and thus more of the rearranged product $(Me_3Si)_2C(SiEt_2Ph)(SiMe_2OM)$ than of the unrearranged $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2OM)$ would be expected. [In the reaction of **2** with $AgBF_4$ in $Et_2O$, which involves rate-determining formation of cation **I**, R = Et, the ratio of rearranged fluoride, $(Me_3Si)_2C(SiEt_2Ph)(SiMe_2F)$, to unrearranged fluoride $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2F)$ is *ca.* 3:2.[3]] Thus the variations in the ratio of $S_N1$ and $S_N2$ processes in the solvolysis of the iodide **2** should be reflected in the ratios of the rearranged to unrearranged products. The results described below show that this is indeed the case, and provide for systems of the type under study the first evidence that migration of a carbon-centred ligand can take place in alcoholysis or hydrolysis, as distinct from reactions with much more powerful electrophiles, such as silver salts and ICl, for which such migrations are firmly established.[2–4]

## Results and Discussion

As will be seen from the discussion, the reactions of the iodide $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2I)$, **2**, with the hydroxylic species MOH, where M = $CF_3CH_2$, Me, or H, each give a mixture of two isomers with mass spectra consistent with simple solvolysis products. It is assumed that one of these is the unrearranged $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2OM)$ [*cf.* the exclusive formation of $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2OM)$ in the corresponding reactions of $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2I)$[1]] and, in the light of much evidence for such 1,3-migrations of the ligand Z in reactions of a range of compounds of the type $(Me_3Si)_2C(SiMe_2Z)(SiR_2I)$,[2–4] that the other is the rearranged species $(Me_3Si)_2C(SiMe_2OM)(SiEt_2Ph)$. (No other possibilities can be realistically considered.) It is further assumed, in the light of much evidence that silver salts promote such migrations,[2–4] that if the presence of a silver salt leads to an increase in the proportion of one of the isomers, then that isomer is the rearranged one. Assignment of the $^1H$ NMR signal from the methyl protons of the $SiMe_2Ph$ group, which was of importance for deciding which was the major isomer, could be confidently made in the light of the corresponding data for the dimethyl compounds $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2OM)$.[1]

*Trifluoroethanolysis.*—After reaction of **2** with a 2.5:1 (v/v) mixture of $CF_3CH_2OH$ and $CHCl_3$ in the presence of $Et_3N$ (to take up the HI generated) at 60 °C for 1 h the solvent was

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evaporated and the organosilicon products extracted into $\mathrm{CDCl_3}$. Analysis by linked gas-liquid chromatography-mass spectrometry (GLC-MS) showed that all of the iodide **2** had reacted and revealed the presence of two isomeric products with the expected composition, in the peak area ratio of *ca.* 5.5:1. (No other products were detected.) The major product had the shorter retention time, and so by analogy with the observations[3] on the corresponding fluorides $\mathrm{(Me_3Si)_2C(SiEt_2Ph)(SiMe_2F)}$ and $\mathrm{(Me_3Si)_3C(SiMe_2Ph)(SiEt_2F)}$ was provisionally assumed to be the rearranged trifluoroethoxide, $\mathrm{(Me_3Si)_2C(SiEt_2Ph)(SiMe_2OCH_2CF_3)}$ and this view was reinforced by the observation that although both isomers had otherwise virtually identical mass spectra the peak of the ion $\mathrm{[Me_2PhSi]^+}$ at *m*/*z* 135 was significantly larger in the case of the less abundant isomer, in which the potential fragment already exists.

The $^{19}$F NMR spectrum of the mixture showed two triplets, centred at −75.5 and −75.1 ppm, in a height ratio of *ca.* 5:1. That the dominant isomer was indeed the rearranged species was confirmed by the $^1$H NMR spectrum of the mixture, which showed peaks at $\delta$ 7.1–7.8 (Ph), 3.6–4.2 ($\mathrm{SiCH_2OCH_2CF_3}$, two sets of quartets), 0.7–1.4 ($\mathrm{SiEt_2}$, two sets of multiplets), 0.55 ($\mathrm{Si}Me_2\mathrm{Ph}$, singlet) and 0.25 ($\mathrm{SiMe_3}$ + $\mathrm{Si}Me_2\mathrm{OCH_2CF_3}$, apparent singlet). [The signal at $\delta$ 0.55 is assigned to the $\mathrm{Si}Me_2\mathrm{Ph}$ protons by comparison with the data for the closely related compound $\mathrm{(Me_3Si)_3C(SiMe_2Ph)(SiMe_2OCH_2CF_3)}$, for which the corresponding signal is at $\delta$ 0.57, and that from the $\mathrm{Si}Me_2\mathrm{OCH_2CF_3}$ protons at $\delta$ 0.14;[1] the signal from the $\mathrm{Si}Me_2\mathrm{Ph}$ protons in the initial iodide **2** is at $\delta$ 0.72.[3]] The ratio of the integral for the $\mathrm{Si}Me_2\mathrm{Ph}$ singlet to that for the Ph multiplet was *ca.* 1:5; if there were no rearrangement this ratio would be 6:5, and the observed ratio indicates a ratio of *ca.* 85:15 for the rearranged to unrearranged species, in line with the conclusions from the GLC-MS and $^{19}$F NMR data.

The results are consistent with the conclusion reached previously that the trifluoroethanolysis of **1** proceeds exclusively by the $\mathrm{S_N1}$ mechanism.[1]

*Methanolysis.*—After reaction of **2** with a 10:1 v/v mixture of MeOH and $\mathrm{CCl_4}$ for 18 h at 60 °C the solvent was removed and the residue taken up in $\mathrm{CDCl_3}$. The $^1$H NMR spectrum was complicated by the presence of a substantial amount of unchanged **2**, and so could not be satisfactorily used for analysis. However, GLC–MS revealed the presence of two isomeric methoxides with the expected composition in *ca.* 65:35 ratio, the major component having the shorter retention time and showing the smaller peak for the ion at *m*/*z* 135 in the mass spectrum, and so probably the rearranged methoxide $\mathrm{(Me_3Si)_2C(SiEt_2Ph)(SiMe_2OMe)}$. No other product was detected.

When the reaction was carried out in the presence of $\mathrm{Ag_2SO_4}$, to promote the generation of the cation **I**, R = Et (see refs. 3 and 4) the $^1$H NMR spectrum was again somewhat complex because of the presence of minor amounts (*ca.* 10% in total) of impurities, probably silanols arising from the presence of traces of water in the methanol. However, GLC–MS revealed the presence of the two isomeric methoxides in a ratio of *ca.* 80:20, and there can be no doubt in this case that the dominant species is the rearranged one. The fact that the ratio is larger than that, *ca.* 65:35, from the reaction in the absence of $\mathrm{Ag_2SO_4}$ is consistent with the conclusion that methanolysis of **1** proceeded partly by the $\mathrm{S_N2}$ process. For **1** the ratio of the contribution from the $\mathrm{S_N1}$ to that from the $\mathrm{S_N2}$ process was estimated to be *ca.* 55:45.[1] Because of the increased steric hindrance at the $\mathrm{SiEt_2I}$ centre in **2**, which would be expected to reduce the rate of the $\mathrm{S_N2}$ more than that of the $\mathrm{S_N1}$ process, the corresponding ratio for **2** could be as low as, say, 70:30, and this would be satisfactorily consistent with the *ca.* 65:35 ratio of rearranged to unrearranged product. In view of the level of experimental uncertainty in the isomer ratios more detailed comparisons would be unwise.

*Hydrolysis.*—A solution of **2** in a 5% (v/v) water–dioxane mixture was kept at 60 °C, with occasional withdrawal of sample for GLC–MS examination. After 100 h no remaining **2** could be detected and the solution was evaporated to dryness and the residue taken up in $\mathrm{CDCl_3}$. The NMR spectrum was consistent with the presence of two isomers, one greatly dominant. The ratio of the integrated signal from the $\mathrm{Si}Me_2\mathrm{Ph}$ protons at $\delta$ 0.50 [compare $\delta$ 0.57 for $\mathrm{(Me_3Si)_3C(SiMe_2Ph)(SiMe_2OH)}$[1]] to that for the (total) aryl protons was *ca.* 4.8:5.0, compared with the 6.5/5.0 expected if there were no rearrangement, indicating that the rearranged and unrearranged silanols were present in *ca.* 20:80 ratio. This could not be confirmed directly by GLC–MS because the two isomers were not resolved. (No other products were detected.) Thus the mixture was treated with acetyl chloride to convert the silanols into acetates, and the mixture was again taken up in $\mathrm{CDCl_3}$. The presence of some residual silanols complicated the $^1$H NMR spectrum, but two peaks from $\mathrm{CH_3CO_2}$ protons, at $\delta$ 2.125 and 2.075, were clearly resolved, and were in a height ratio of *ca.* 4:1. Examination by GLC–MS confirmed the presence of some remaining silanol(s), but there were two major peaks for the acetates, in *ca.* 4:1 area ratio. The dominant isomer in this case had the longer retention time, consistent with its being the unrearranged $\mathrm{(Me_3Si)_2C(SiMe_2Ph)(SiEt_2OCOMe)}$. (The ratio of the isomeric acetates may not exactly mirror that of the silanols since these may not have been converted into acetates to precisely the same extent, but this effect is likely to be small.)

The validity of the identification of the dominant product of the hydrolysis as the unrearranged silanol was confirmed when the reaction was carried out (for a shorter time) in the presence of $\mathrm{Ag_2SO_4}$. In this case the ratio of the integrated signal from the $\mathrm{Si}Me_2\mathrm{Ph}$ to that for the total aryl protons was *ca.* 1:2, consistent with a ratio of *ca.* 60:40 of rearranged to unrearranged silanol. After conversion of the silanols into acetates, the ratio of the areas of the peaks from GLC–MS was *ca.* 40:60 compared with the previous 80:20, and the resonances from the $\mathrm{CH_3CO_2}$ protons at $\delta$ 2.125 and 2.075 were in a height and integration ratio of *ca.* 45:55. There can be no doubt that the dominant product from the reaction in the presence of silver salt is the rearranged species, and so that from the reaction in its absence is confirmed as the unrearranged species. The proportion of the rearranged product, *ca.* 20%, may appear rather high in the light of the estimate of *ca.* 10% for the contribution of the $\mathrm{S_N1}$ process in the hydrolysis of **1**,[1] but this difference is not significant in view of the uncertainty in that estimate and in all of the experimentally observed ratios, and also because (i) the contribution of the $\mathrm{S_N1}$ process would be expected to be somewhat larger for **2** than for **1**, as noted for the methanolysis, and (ii) the reaction conditions used in the present study were somewhat different from those used in the rate studies.

## Conclusions

The proportions of rearranged products from the various solvolyses of **2** nicely confirm the earlier conclusions based on rate studies that the trifluoroethanolysis of **1** proceeds exclusively by the ionization, $\mathrm{S_N1}$, process, methanolysis by a mixture of $\mathrm{S_N1}$ and $\mathrm{S_N2}$ processes, with the former slightly predominant, and hydrolysis very predominantly by the $\mathrm{S_N2}$ process.

## Experimental

*Materials.*—The preparation of **2** was described previously.[3] 2,2,2-Trifluoroethanol was refluxed over, and distilled from, $CaH_2$ and stored over a 4 Å molecular sieve. Methanol was Aldrich Gold Label Anhydrous grade.

*Spectra and chromatography.* The $^1H$ NMR spectra were recorded at 360 MHz on a Bruker WM360 spectrometer with $CDCl_3$ as solvent and lock and residual $CHCl_3$ as standard. The $^{19}F$ NMR spectra were recorded at 75.4 MHz on a Bruker WP80 FT spectrometer in $CDCl_3$. Shifts are in ppm relative to $CFCl_3$. *J* values are given in Hz.

For GLC–MS, a 2 m column of OV-17 on 100–120 mesh Gas Chrom. Q was used, with temperature programming from 150°–250 °C at 8 °C $min^{-1}$. Mass spectra were by electron impact at 70 eV.

*Trifluoroethanolysis.*—2,2,2-Trifluoroethanol (1.00 $cm^3$) was added to a solution of **2**, (23 mg, *ca.* $5.7 \times 10^{-2}$ mmol) in $CHCl_3$ (0.40 $cm^3$) containing $Et_3N$ (1.16 mg, *ca.* $12 \times 10^{-2}$ mmol) and the mixture was kept at 60 °C for 1 h, after which examination by GLC showed that no **2** remained. The solution was evaporated to dryness under reduced pressure and the residue extracted with $CDCl_3$ (0.5 $cm^3$). Analysis by GLC–MS revealed the presence of two isomeric trifluoroacetates in a peak area ratio of *ca.* 5.5:1, the major component having the shorter retention time and giving a smaller peak at *m/z* 135 in the mass spectrum which was otherwise essentially identical to that of the other component. [Main ions: *m/z* 463 (M − Me), 449 (M − Et, base peak) 369, 349, 175, 135 ($Me_2PhSi$) and 73 ($Me_3Si$).]

The $^{19}F$ NMR spectrum of the solution showed two triplets ($J = 8.7$), at −75.5 and −75.1 ppm, with peaks in a height ratio of *ca.* 5:1. The $^1H$ NMR spectrum showed resonances at $\delta$ 0.25 (s, $SiMe_3$), 0.55 (s, $SiMe_2Ph$), 0.7–1.4 (two sets of multiplets, $SiEt_2$), 3.6–4.2 (two sets of quartets, $CH_2CF_3$), and 7.1–7.8 (m, Ph). (The missing peak for the $SiMe_2OCH_2CF_3$ protons was hidden under the $Me_3Si$ signal.) The ratio of the integral for the signal from the $SiMe_2Ph$ protons to that for the signal from all Ph protons was *ca.* 1:5.

*Methanolysis.*—(i) Methanol (0.50 $cm^3$) was added to a solution of **2** (25 mg) in $CCl_4$ (0.050 $cm^3$) and the mixture was kept at 60 °C for 18 h. The solvent was then evaporated off under reduced pressure and the residue taken up in $CDCl_3$ (0.5 $cm^3$). Analysis by GLC showed that much unchanged **2** remained, and because of this the $^1H$ NMR spectrum was too complex for analysis. Analysis by GLC–MS revealed the presence of two isomeric methoxides [*m/z* 385 (M-Me), 381 (M-Et, base peak), 175, 135, 73] in a peak area ratio of *ca.* 65:35, the major component having the shorter retention time and giving the smaller peak at *m/z* 135 in the mass spectrum.

(ii) The reaction was carried out as above but in the presence of $Ag_2SO_4$ (2 mg). Examination by GLC–MS showed that a little unchanged **2** remained (probably because of coating of the $Ag_2SO_4$ with AgI) and that there were again minor products (< 10%; probably silanols) in addition to the two methoxides, which were present in a ratio of 75:25, the major component again having the shorter retention time and giving the smaller peak at *m/z* 135. Because of the presence of unchanged substrate and the minor additional products the $^1H$ NMR spectrum could not be used satisfactorily for analysis.

*Hydrolysis.*—(i) A solution of **2** (25 mg) in 5% (v/v) water–dioxane (1.0 $cm^3$) was kept at 60 °C for 100 h after which GLC analysis showed that no unchanged **2** remained. The solvent was evaporated under vacuum and the residue taken up in $CDCl_3$ (*ca.* 1.0 $cm^3$). Analysis of a sample by GLC gave only one peak for the silanol products. The $^1H$ NMR spectrum showed resonances at $\delta$ 0.13 (poorly resolved, probably $SiMe_2OH$), 0.17 (18 H, s, $SiMe_3$); 0.50 (4.8 H, s, $SiMe_2Ph$), 0.61–1.10 (10 H, m, Et) and 7.20–7.73 (5 H, m, Ph).

The solution was evaporated to dryness and the residue treated with acetyl chloride (5 $cm^3$) for 12 h at 60 °C, after which the acetyl chloride was evaporated off under reduced pressure and the residue taken up in $CDCl_3$ (*ca.* 0.5 $cm^3$). Analysis by GLC–MS showed that some of the silanols still remained, but there were two peaks for the isomeric acetates, in 4:1 area ratio, the major component having the longer retention time. In this case there was no significant difference in the heights of the peak at *m/z* 135 in the mass spectra of the isomers; [*m/z* 381 (M − Me), 367 (M − Et, base peak), 352, 289, 135, 73. The $^1H$ NMR spectrum was complex because of the presence of the silanols, but there were two $CH_3CO_2$ signals, at $\delta$ 2.125 and 2.075, in *ca.* 4:1 height and integration ratio.

(ii) The hydrolysis was repeated but in the presence of $Ag_2SO_4$ (2 mg) and for 30 h at 60 °C. Again analysis by GLC gave only one peak for the hydroxides, but the $^1H$ NMR spectrum of the solution was as expected for a mixture of the two isomers. The silanols were converted into acetates as before, and the isomeric acetates shown by GLC and GLC–MS to be present in a ratio of *ca.* 60:40, the major component having the shorter retention time. The signals from the $CH_3CO_2$ protons at $\delta$ 2.125 and 2.075 were in *ca.* 45:55 height and integration ratio.

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