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Reactions of compounds of the type $(Me_3Si)_2C(SiMe_2C_6H_4Y)(SiMe_2X)$ with trifluoroacetic acid

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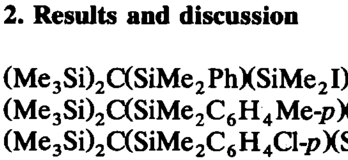
Abstract

The iodides $(Me_3Si)_2C(SiMe_2C_6H_4Y)(SiMe_2I)$, with Y = H, *p*-OMe, and *p*-Cl, react with trifluoroacetic acid at 35°C to give the bis(trifluoroacetate) $(Me_3Si)_2C(SiMe_2O_2CCF_3)_2$, **8**. The initial reaction involves solvolysis at the Si–I bond to give HI and $(Me_3Si)_2C(SiMe_2C_6H_4Y)(SiMe_2OCCF_3)$, and the HI then cleaves the Si–aryl bond in the latter and in the starting material to give $(Me_3Si)C(SiMe_2I)(SiMe_2O_2CCF_3)$ and $(Me_3Si)_2C(SiMe_2I)_2$, which then undergo further solvolysis, with anchimeric assistance by γ-O_2CCF_3 or γ-I to leaving of I^-. In the case of the corresponding reaction of the bromide $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2Br)$ the dibromide is clearly seen as an intermediate. In keeping with the above, when Et_3N is present to neutralize the HI the reaction of $(Me_3Si)_2C(SiMe_2C_6H_4Cl\text{-}p)(SiMe_2I)$ gives only the expected $(Me_2Si)_2C(SiMe_2C_6H_4Cl\text{-}p)(SiMe_2O_2CCF_3)$. The reactions of the compounds $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2OR)$, R = Me or H, also give **8**, but the initial reaction is cleavage of the Si–Ph bond by CF_3CO_2H, and it is suggested that this process is assisted by initial protonation of the OR group followed by transfer of the proton to the nearby *ipso* carbon atom of the phenyl group.

1. Introduction

We recently described the results of a study of the solvolysis of the iodides $(Me_3Si)_2C(SiMe_2C_6H_4Y)(SiMe_2I)$ (Y = *m*-CF_3, *p*-Cl, H, *p*-Me, and *p*-OMe) in $(CF_3)_2CHOH$, CF_3CH_2OH, MeOH, and aqueous-dioxane [1,2]. We showed that the reactions with the fluorinated alcohols (which are relatively acidic and electrophilic) proceed by an ionization (S_N1) mechanism, anchimeric assistance by the aryl group in the rate-determining step of leaving of I^- leading to formation of a 1,3-bridged cation (**I**), which is then rapidly attacked by the solvent ROH at the α- or γ-silicon atom to give $(Me_3Si)_2C(SiMe_2C_6H_4Y)(SiMe_2OR)$. In MeOH this type of process was accompanied by a direct bimolecular (S_N2) attack of the solvent on the Si–I bond, and in aqueous dioxan this was the greatly dominant process. We now report on the reactions of some compounds of the type $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2X)$ and related species (compounds **1–6**) with trifluoracetic acid. In this much more acidic and more electrophilic medium even the iodide $(Me_3Si)_3CSiMe_2I$ undergoes reaction by the S_N1 mechanism (as shown by the fact that the closely related compound $(Me_3Si)_3CSiEt_2I$ reacts to give the rearranged product $(Me_3Si)_2C(SiEt_2Me)(SiMe_2O_2CCF_3)$ along with the normal product $(Me_3Si)_3CSiEt_2O_2CCF_3$ [3]).



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2. Results and discussion

$(Me_3Si)_2C(SiMe_2Ph)(SiMe_2I)$	**1**
$(Me_3Si)_2C(SiMe_2C_6H_4Me\text{-}p)(SiMe_2I)$	**2**
$(Me_3Si)_2C(SiMe_2C_6H_4Cl\text{-}p)(SiMe_2I)$	**3**
$(Me_3Si)_2C(SiMe_2Ph)(SiMe_2Br)$	**4**
$(Me_3Si)_2C(SiMe_2Ph)(SiMe_2OMe)$	**5**
$(Me_3Si)_2C(SiMe_2Ph)(SiMe_2OH)$	**6**

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$(Me_3Si)_2C(SiMe_2Ph)(SiMe_2O_2CCF_3)$	**7**
$(Me_3Si)_2C(SiMe_2O_2CCF_3)_2$	**8**
$(Me_3Si)_2C(SiMe_2I)_2$	**9**
$(Me_3Si)_2C(SiMe_2Br)_2$	**10**

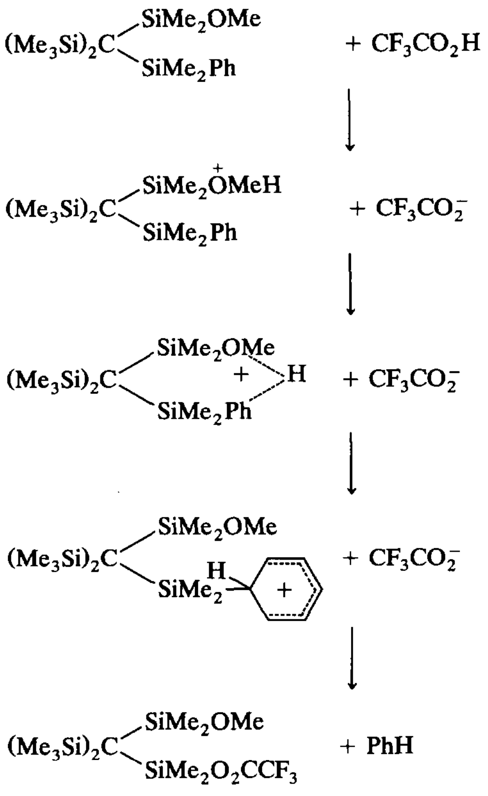
When the iodide **1** was treated with CF_3CO_2H at 35°C the ^1H NMR spectrum showed that after 1.5 h only the bis(trifluoroacetate) **8** was present. The same result was obtained when the related iodide **2** was treated with the acid for 0.5 h at 35°C. It appears (see discussion below) that the initial reaction is solvolysis at the Si–I bond, though this must, as would be expected, be anchimerically assisted by the γ-aryl group, since the solvolysis of the compound $(Me_3Si)_3CSiMe_2I$ occurs much more slowly even in the refluxing acid [3]. Thus $(Me_3Si)_2C(SiMe_2C_6H_4Y)(SiMe_2O_2CCF_3)$ would be formed along with HI, and the latter, which is a very strong acid in CF_3CO_2H (*cf.* ref. 4) would cleave the Si–aryl bond in the starting material to give the diodide $(Me_3Si)_2C(SiMe_2I)_2$, **9**, and that in $(Me_3Si)_2C(SiMe_2C_6H_4Y)(SiMe_2O_2CCF_3)$ to give the bis(trifluoroacetate) $(Me_3Si)_2C(SiMe_2O_2CCF_3)_2$, **8**. The diiodide would then undergo solvolysis, with anchimeric assistance by one iodide ligand to leaving of the other to give $(Me_3Si)_2C(SiMe_2O_2CCF_3)(SiMe_2I)$, and the latter rapid solvolysis, assisted by the γ-O_2CCF_3 ligand to give **8** (*cf.* ref. 5). (In the case of the corresponding reaction of the related bromide $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2Br)$ the dibromide $(Me_3Si)_2C(SiMe_2Br)_2$ was clearly detected as an intermediate, as described below.)

The alternative possibility had to be considered that the initial reaction involved cleavage of the Si–aryl bond by CF_3CO_2H, since $(Me_3Si)_3CSiMe_2Ph$ is cleaved by the acid, though relatively slowly, with a half-life of *ca.* 1 h at 37.5°C [6]. However, when the less reactive *p*-chloro-derivative **3** was examined it was found that whereas the reaction with CF_3CO_2H alone gave exclusively **8** after 28 h, when 2 equivalents of Et_3N were present the product (as confirmed by analysis by linked GLC–mass spectrometry) was $(Me_3Si)_2C(SiMe_2C_6H_4Cl\text{-}p)(SiMe_2O_2CCF_3)$, the base having inhibited the attack of HI on the Si–aryl bond. Furthermore $(Me_3Si)_2C(SiMe_2C_6H_4Cl\text{-}p)(SiMe_2O_2CCF_3)$ was found not to react at a significant rate with CF_3CO_2H, evidently as a result of the deactivation arising from the electron withdrawal by the *p*-chloro-substituent (*cf.* ref. 7).

In keeping with the above picture, when the bromide **4** was treated with CF_3CO_2H, monitoring by ^1H NMR spectroscopy revealed clearly that the dibromide **10** was formed in substantial quantity as an intermediate. Thus after 20 min at 35°C half of the starting material had disappeared and the dibromide **10** and the bis(trifluoracetate) **8** constituted *ca.* 20 and 30%, respectively, of the mixture. After 1.6 h no **4** was detectable and the solution contained *ca.* 35% of **10** and 65% of **8**, but after 19 h only the latter was present. Thus initial solvolysis at the Si–Br bond was followed by slower cleavage of the Si–Ph bond by the HBr generated. It is of interest that this cleavage involves formation of an Si–Br bond rather than an $Si\text{–}O_2CCF_3$ bond.

The opposite sequence of events was observed in the reactions of the methoxide **5** and hydroxide **6** with CF_3CO_2H at 35°C. Examination of the solutions after 5 and 15 min, respectively, showed that in both cases only the bis(trifluoroacetate) **8** was present. The possibility that the initial reaction involved reaction at the Si–O bond to give $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2O_2CCF_3)$, **7**, with subsequent cleavage of the Si–Ph bond, was ruled out by the observation that when **7** itself was treated with CF_3CO_2H at 35°C, after 18 h only 60% of **7** had reacted, to give the expected **8**.

It should be noted that the reaction of the methoxy compound **5** (and also that of the hydroxy analogue **6**) with CF_3CO_2H is much faster than that of $(Me_3Si)_3CSiMe_2Ph$, which, as noted earlier, has a half-life of *ca.* 1 h at 37.5°C [6], and thus the γ-OMe group evidently markedly facilitates the cleavage of the Si–Ph bond, as it does that of an Si–Me bond in $(Me_3Si)_3CSiMe_2OMe$ [6]. It is thought that in the reaction of $(Me_3Si)_3CSiMe_2Ph$ the rate determining step is the protonation at the *ipso* carbon atom of the aryl group [6]. It is difficult to see how the presence of the γ-OMe group in **5** could *directly* assist such protonation, to cause **5** to react much more rapidly than $(Me_3Si)_3CSiMe_2Ph$. To account for the abnormal ease of cleavage of an Si–Me bond in $(Me_3Si)_3CSiMe_2OMe$ we suggested a synchronous process in which nucleophilic attack by the γ-OMe group at the Si–Me bond is concerted with proton transfer to carbon and breaking of the Si–Me bond [6], and a similar scheme could be envisaged for the reaction of **5**. However, such a process, involving concerted (though not necessarily fully synchronous) making or breaking of five bonds, is inherently unattractive, and we have never had much enthusiasm for our suggestion of it, and it is appropriate to consider the possibility that the γ-OMe group facilitates the reactions of **5** and $(Me_3Si)_3CSiMe_2OMe$ by an effect other than the usual anchimeric assistance to give a methoxy-bridged cation [8]. An attractive possibility can be based on the fact that (i) the γ-OMe group in these highly crowded systems is constrained to lie very close to another silicon centre (*cf.* ref. 9), and (ii) protonation of the OMe group will occur very readily to give a small stationary concentration of the protonated species. The function of the OMe group



Scheme 1. A suggested sequence whereby the γ-OMe group in $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2OMe)$ assists cleavage of the Si–Ph bond by trifluoroacetic acid.

could thus be to act as a carrier to pass the proton to the carbon atom of a nearby Si–Me or Si–Ph bond with breaking of that bond. In the case of **5** there could be a short-lived protonated-aryl intermediate, as shown in Scheme 1, but this is not a necessary feature.

3. Experimental details

3.1. Materials

The route to the iodides **1**–**3** has been outlined [1]. Details of these preparations and those of **4**–**7** will be given elsewhere. Authentic samples of $(Me_3Si)_2C(SiMe_2O_2CCF_3)_2$, **8** [5a], and $(Me_3Si)_2C(SiMe_2Br)_2$, **10** [10], were available.

3.2. Spectra

The ^1H NMR spectra were recorded at 90 MHz on a Perkin Elmer R32 NMR spectrometer.

3.3. Reactions of the iodides 1–3

The iodide (6 mg) was dissolved in two drops (*ca.* 0.02 cm^3) of CH_2Cl_2 in an NMR tube. Trifluoroacetic acid (*ca.* 0.50 cm^3) was added and the tube was firmly capped, shaken briefly, and placed in a thermostat bath at 35.0 ± 0.2°C. In the case of **1** after 1.5 h, and of **2** after 0.5 h, the spectrum was recorded and revealed that in each case only $(Me_3Si)_2C(SiMe_2O_2CCF_3)_2$, **8**, was present. (Addition of an authentic sample confirmed the identity of the product.) In the case of **3** the spectrum was recorded at intervals, and after 18 h only **8** was present.

In a separate experiment the iodide **3** (6 mg, 0.012 mmol) was dissolved in $CDCl_3$ (500 μl) containing two molar equivalents of Et_3N. Trifluoroacetic acid (0.50 cm^3) was added and the tube was sealed, briefly shaken, and placed in the probe of the spectrometer at 35.0°C. The spectrum was recorded at intervals up to *ca.* 60% completion of the reaction and the heights S and P of the peaks from the Me_3Si protons in the starting material **3** and product $(Me_3Si)_2C(SiMe_2C_6H_4Cl\text{-}p)(SiMe_2O_2CCF_3)$, respectively, were determined. A plot of ln [S/(S + P)] against time gave a good straight line, the slope of which yielded a first order rate constant of 1.1×10^{-6} s^{-1} ($t_{1/2}$ 17.5 h). The tube was then transferred to a bath at 35°C, and after a total reaction time of 6 days the solution was evaporated to dryness under reduced pressure. The solid residue was shown to be $(Me_3Si)_2C(SiMe_2C_6H_4Cl\text{-}p)(SiMe_2CCF_3)$, δ_H (CCl_4 with 5% CH_2Cl_2) 0.30 (18H, s, $SiMe_3$), 0.42 (6H, s, $SiMe_2O$), 0.59 (6H, s, $SiMe_2$aryl), and 7.18–7.71 (4H, m, C_6H_4). Linked GLC–mass spectrometry (EI) (3% OV17 on 100–120 mesh GasChrom G) gave only one chromatographic peak, with mass spectral peaks at *m/z* 483 (45%, M – Me), 433 (32, M – MeCl – Me), 297 (60, M – $SiMe_2O_2CCF_3$ – Me), 275 (20), 215 (70), 205 (75), 169 (60, $SiMe_2C_6H_4Cl$), 139 (90), 73 (100, Me_3Si).

3.4. Reaction of the bromide 4

The bromide **4** (6 mg) was dissolved in CCl_4 (*ca.* 0.02 cm^3). Trifluoracetic acid (0.50 cm^3) was added and the tube was firmly capped, briefly shaken, and placed in a thermostat bath at 35.0°C. The ^1H NMR spectrum was recorded at intervals and the heights of the signals from the Me_3Si peaks of **4**, **10**, and **8** were measured and taken to give the ratios of **4**, **10**, and **8** as follows: 0.27 h, 94/6/0; 0.60 h, 63/15/22; 0.73 h, 50/20/30; 0.80 h, 43/21/36; 1.0 h, 26/27/47; 1.20 h, 16/31/53; 1.40 h, 11/32/57; 1.6 h, 5/33/62; 1.8 h, 0/34/66; 19 h, 0/0/100. An authentic sample of the dibromide **10** was used to confirm the identity of the intermediate.

3.5. Reactions of $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2X)$ (X = OMe or OH), 5 and 6

A sample (6 mg) of **5** or **6** was dissolved in CH_2Cl_2 (0.02 cm^3) in an NMR tube, CF_3CO_2H (0.50 cm^3) was added and the tube was firmly capped, shaken briefly, and placed in the probe of the spectrometer at 35.0°C.

After 5 min in the case of **5** and 15 min in that of **6** the ^1H NMR spectrum showed that only the bis(trifluoroacetate) **8** was present.

3.6. *Reaction of* $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2O_2CCF_3)$, *7*

A sample of **7** (5 mg) was placed in an NMR tube, CF_3CO_2H (0.50 cm^3) was added, and the tube was capped, shaken, and kept in a bath at 35°C. After 18 h the ^1H NMR spectrum showed the presence of unchanged **7** (60%) and the bis(trifluoracetate) **8** (40%).

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