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Preliminary communication

1,3-MIGRATION OF CHLORIDE AND AZIDE SUBSTITUENTS WITHIN ORGANOSILICON CATIONS, AND ANCHIMERIC ASSISTANCE BY THE AZIDO GROUP

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Summary

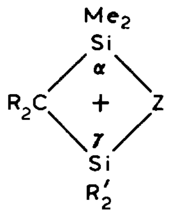
Migration of the Cl substituent takes place when $(Me_3Si)_2C(SiMe_2Cl)(SiEt_2I)$ or $(Me_3Si)_2C(SiEt_2Cl)(SiMe_2I)$ reacts with $AgBF_4$, the product in each case being a mixture of $(Me_3Si)_2C(SiEt_2Cl)(SiMe_2F)$ and $(Me_3Si)_2C(SiEt_2F)(SiMe_2Cl)$, and analogous migration of N_3 occurs in the corresponding reaction of $(Me_3Si)_2C(SiEt_2N_3)(SiMe_2Br)$. Anchimeric assistance by the N_3 group facilitates the solvolysis of $(Me_3Si)_2C(SiMe_2N_3)(SiMe_2Br)$.

It has previously been shown that in abstraction of the group X from compounds of the type $R_2C(SiMe_2Z)(SiR'_2X)$ ($R = Me_3Si$ throughout) by silver salts (as in reactions with various other electrophiles) 1,3-migration of the Z group can take place, to give the rearranged product $R_2C(SiMe_2Y)(SiR'_2Z)$, either exclusively or along with the unrearranged product $R_2C(SiMe_2Z)(SiR'_2Y)$ [1]. Such reactions are thought to involve formation of the bridged species (I), which is then attacked by the nucleophile Y^- at either the α- or γ-Si (attack at the least hindered centre usually being favoured) and rearrangement has been shown to occur for Z = Me [2], OMe [3], and $CH{=}CH_2$ [4]. Calculations on model cations indicate the bridging as in I should be very effective for Z = Cl [5], and we have now demonstrated that the corresponding migration of Cl takes place, as does that of N_3.

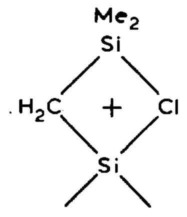
Seemingly unaware of the earlier prediction of 1,3-Si to Si-bridging by Cl, Pope and Jones have interpreted the mass spectra of $(Me_3SiCH_2)_nSiCl_{4-n}$ compounds in terms of significant stability of the four-membered ring species of type II [6].

Compounds 1–4 were made by the routes shown in Scheme 1.

When compound 1 was treated with $AgBF_4$ in CH_2Cl_2 for 5 min at room temperature the product after work-up (evaporation, extraction of the residue with pentane, filtration and evaporation of the extract) gave ^1H and ^{19}F NMR spectra which showed it to be an ca. 1/3 mixture of the rearranged fluoride $R_2C(SiMe_2Cl)(SiEt_2F)$ and the unrearranged $R_2C(SiMe_2F)(SiEt_2Cl)$. (The ^1H



(I)



(II)

NMR. signals at δ 0.33(s), 0.49 (d, *J* 7.5 Hz), 0.66 (d, *J* 0.6 Hz) and 0.94–1.18(m) were attributed to $SiMe_3$, $SiMe_2F$, $SiMe_2Cl$, and $SiEt_2$ protons, respectively, and were in 13/3/1/8 integration ratio; ^{19}F signals (in CCl_4 relative to $CFCl_3$) at δ −143.0 (m, *J* 7.3 Hz) and −160.2 ppm (m, *J* 10.7 Hz) were attributed to $SiMe_2F$ (cf. δ(F) −144.7 ppm for $R_3C(SiMe_2F)$) and $SiEt_2F$ (cf. −160.4 for $R_3C(SiEt_2F)$) and were in a 1/3 integration ratio. Linked GLC-mass spectrometry gave only one peak, with a mass spectrum consistent with either of the isomeric fluorides [m/z 341 ($[M-\text{Me}]^+$), 327 ($[M-\text{Et}]^+$). A similar reaction carried out in Et_2O gave virtually identical results except for the formation of small amounts of side-products that gave no ^{19}F NMR signals.

When **2** was treated in CH_2Cl_2 with $AgBF_4$, $R_2C(SiMe_2Cl)(SiEt_2F)$ and $R_2C(SiMe_2F)(SiEt_2Cl)$ were again formed, but in ca. 1/2 ratio (i.e., in this case the rearranged product predominated), demonstrating that the cation I (R′ = Et, Z = Cl) can be generated from both directions. Although the observed product isomer ratios are only approximate, it seems likely that they do differ somewhat for the reactions of **1** and **2**, whereas on the simplest picture of the reaction, with ions of type I becoming fully isolated before reacting with the nucleophile, **1** and **2** would be expected to give rise to the same product ratio. However it is possible, for example,

$$\text{(a) } R_2CCl_2 \xrightarrow{(i)(ii)} R_2C(Cl)(SiMe_2H) \xrightarrow{(iii)(iv)} R_2C(SiEt_2Cl)(SiMe_2H) \xrightarrow{(v)} R_2C(SiEt_2Cl)(SiMe_2I)$$

(1)

Reagents: (i) BuLi in hexane/THF/Et_2O/pentane at −110°C; (ii) Me_2SiHCl; (iii) BuLi in hexane/THF/Et_2O/pentane at −100°C; (iv) Et_2SiCl_2; (v) I_2 in CCl_4.

$$\text{(b) } R_2CCl_2 \xrightarrow{(i)(ii)} R_2C(Cl)(SiEt_2H) \xrightarrow{(iii)(iv)} R_2C(SiMe_2Cl)(SiEt_2H) \xrightarrow{(v)} R_2C(SiMe_2Cl)(SiEt_2I)$$

(2)

Reagents: (i) As in (a); (ii) Et_2SiHCl; (iii) as in (a); (iv) Me_2SiCl_2; (v) I_2 in CCl_4.

$$\text{(c) } R_2C(SiMe_2H)(SiEt_2Cl) \xrightarrow{(i)} R_2C(SiEt_2N_3)(SiMe_2H) \xrightarrow{(ii)} R_2C(SiEt_2N_3)(SiMe_2Br)$$

(3)

Reagents: (i) NaN_3 in MeCN; (ii) Br_2 in CCl_4.

$$\text{(d) } R_2C(Cl)(SiMe_2Br) \xrightarrow{(i)} R_2C(Cl)(SiMe_2N_3) \xrightarrow{(ii)(iii)} R_2C(SiMe_2N_3)(SiMe_2Cl)$$

(4)

Reagents: (i) NaN_3 in MeCN; (ii) BuLi in THF/Et_2O/pentane at −110°C; (iii) Me_2SiCl_2 at −80°C.

SCHEME 1

the BF_4^- liberated near the Si centre from which I^- is abstracted is able to attack that centre to some extent before diffusing away; this would tend to give less of the rearranged product in both cases than would be expected on simple steric grounds.

The azide **3** reacted correspondingly with $AgBF_4$ in CH_2Cl_2 during 5 min at room temperature to give a 1/3 mixture of the rearranged $R_2C(SiMe_2N_3)(SiEt_2F)$ and the unrearranged $R_2C(SiMe_2F)(SiEt_2N_3)$. The ^{19}F NMR spectum (in CCl_4) consisted of two multiplets, at δ −143.4 ($SiMe_2F$) and −160.3 ($SiEt_2F$), in 3/1 integration ratio; the ^1H NMR spectrum (360 MHz) in CCl_4) showed signals at δ 0.289 (d, J 0.5 Hz), 0.293 (d, J 0.4 Hz), 0.45 (d, J 7.4 Hz), and 0.52 (d, J 0.5 Hz), in 2/6/3/1 integration ratio, assigned to $SiMe_3$, $SiMe_3$, $SiMe_2F$, and $SiMe_2N_3$ protons, respectively, along with a complex multiplet at δ 0.88–1.25 from the $SiEt_2$ protons. Linked GLC-mass spectrometry gave only one peak, with a mass spectrum consistent with either isomeric product; m/z 348 ($[M-\mathrm{Me}]^+$), 334 ($[M-\mathrm{Et}]^+$).

Since the Cl and N_3 ligands bridge effectively in cations of type I it was to be expected that they would provide substantial anchimeric assistance to the leaving of the group X in compounds of the type $R_2C(SiMe_2Z)(SiMe_2X)$ ($Z = Cl$ or N_3). This was shown to be the case for the N_3 ligand in the reactions of $R_2C(SiMe_2N_3)(SiMe_2Br)$ (**4**), with MeOH and CF_3CH_2OH. In the reactions at 35°C with MeOH in the presence of three equivalents of Et_3N the half life is ca. 100 min, and the product is $R_2C(SiMe_2N_3)(SiMe_2OMe)$. (In the absence of Et_3N the rate is a little higher and the reaction proceeds further to give $R_2C(SiMe_2OMe)_2$, these effects being attributable to assistance by the formed HBr to the leaving of Br^- and N_3^-). In the presence of 0.03, 0.06, and 0.12 M NaOMe (but without the Et_3N) the half lives are ca. 115, 93, and 89 min, respectively; i.e. the NaOMe has only a small effect, which indicates that the reaction is not of the S_N1 type. Furthermore the reaction with the less nucleophilic but more electrophilic alcohol CF_3CH_2OH is much faster, the half life being very roughly 0.5 min, so that the reaction is > 150 times as fast as that with MeOH, which indicates that the solvolysis is of the S_N1 type, involving rate-determining formation of the cation I ($R' = Me$, $Z = N_3$). Compound **4** is very much more reactive than R_3CSiMe_2Br, probably by a factor of at least 10^4 since even the *iodide* R_3CSiMe_2I has a half life of ca. 13 days in MeOH at 50°C and reacts even less readily with CF_3CH_2OH [7]; the actual factor is probably much larger. However, the assistance by the N_3 group, although much larger than that by a vinyl group, is substantially smaller than that by an OMe group, since **4** is markedly less reactive than $R_2C(SiMe_2OMe)(SiMe_2Br)$ towards MeOH, the half life for the latter bromide being only ca. 17 min even in 9/1 dioxane/MeOH containing 0.05 M NaOMe.

As expected from the above analysis, in reactions with KSCN or KOCN in MeCN, which are believed to involve direct bimolecular substitution, so that the anchimeric assistance cannot operate, **4** is not especially reactive, reacting only ca. 17 times as rapidly as R_3CSiMe_2Br, this factor being similar to that between $R_2C(SiMe_2OMe)(SiMe_2Cl)$ and R_3CSiMe_2Cl.

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