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COMPARISONS OF THE REACTIVITIES OF THE TRI-t-BUTYL- AND TRIS(TRIMETHYLSILYL)METHYL-SILICON COMPOUNDS *

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Summary

Comparisons of the reactions of t-Bu_3SiX (X usually I, but in some cases OSO_2CF_3 or Cl) and the corresponding $TsiMe_2X$ species (Tsi = $(Me_3Si)_3)C$) have led to the following conclusions: (a) Under conditions in which $TsiSiMe_2I$ is thought to react via a silicocationic intermediate (mainly, solvolysis in CF_3CO_2H or reactions with silver salts), this iodide is much more reactive than t-Bu_3SiI. (b) The reactivity difference between the two iodides is markedly smaller in reactions with alkali metal salts, i.e. S_N2 processes, the $TsiSiMe_2I$ commonly being ca. 3–8 times the more reactive. (c) In methanolysis and hydrolysis under conditions in which an S_N2-intermediate mechanism may operate, the differences in reactivity between $TsiSiMe_2X$ and t-Bu_3SiX compounds (X = I or OSO_2CF_3) vary considerably with the medium, with the former usually, though not always, the more reactive, but again the differences are much smaller than those in the reactions mentioned under (a) in which the ease of breaking of the Si–X bond is the greatly dominant factor. (d) The differences between the reactivities of iodides and the corresponding chlorides in these highly crowded systems are smaller in reactions in which participation by the nucleophile is important than in those in which the ease of ionization of the Si–X bond is dominant; in reaction with NaN_3, KOCN or KSCN in MeCN, t-Bu_3SiCl is more reactive than t-Bu_3SiI.

Introduction

Several studies of the behaviour of tris(trimethylsilyl)methyl ("trisyl") derivatives of silicon have been carried out in this laboratory in recent years [1–9]. Such derivatives show some special features arising from the particular composition of the

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* Dedicated to Professor Makoto Kumada in recognition of his outstanding contributions to organosilicon chemistry, and in appreciation of our friendship over many years.

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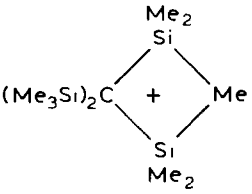
trisyl group (denoted by Tsi): e.g. the loss of Me_3SiF on thermolysis of $TsiSiPh_2F$ [3], and the migration of a Me group in reactions of $TsiSiR_2X$ species thought to proceed via silicocation intermediates of type **A** [1,4,7–9]. Other interesting features, however, arise essentially from the bulk of the trisyl ligand, which greatly inhibits the direct attack of nucleophiles at silicon (the ease of which dominates the reactions of ordinary silicon-functional organosilicon compounds), and this allows observation of reactions and mechanisms which would otherwise be obscured; e.g. the photo-induced [9] and the oxidatively-assisted [8] solvolysis of the iodides $TsiSiR_2I$ (R = Ph or Me). The studies had reached a stage at which it seemed appropriate to examine the behaviour of another type of highly sterically-hindered organosilicon species, viz. $t\text{-}Bu_3SiX$ compounds, in the light of the accumulated knowledge of the trisyl compounds. Much information about the behaviour of $t\text{-}Bu_3SiX$ species was available [10–12], especially from the work of Weidenbruch and his colleagues [10], but it was thought of interest to examine those species under reaction conditions comparable to those used for the trisyl compounds, and the results of such an examination are described below. We have already shown that $t\text{-}Bu_3SiI$ undergoes the same type of reaction as $TsiSiMe_2I$, but more slowly, on treatment with *m*-chloroperoxybenzoic acid in methanol [8].

$t\text{-}Bu_3SiI$ (I)

$t\text{-}Bu_3SiOSO_2CF_3$ (II)



(A)

Results

1. Reactions with silver salts

(a) The reaction between $t\text{-}Bu_3SiI$, (I), and AgO_2CCH_3 in refluxing CH_3CO_2H was monitored by ^1H NMR spectroscopy, and found to be ca. 50% complete after 2 h, 85% complete after 5 h, and effectively complete after 8 h, the product being the expected $t\text{-}Bu_3SiO_2CCH_3$. The reaction is evidently much slower than that of $TsiSiPh_2I$, which was complete within 7 min (the product being the rearranged acetate $(Me_3Si)_2C(SiPh_2Me)(SiMe_2O_2CCH_3)$), and $TsiSiPh_2I$ is less reactive than $TsiSiMe_2I$ in this type of reaction [4].

When $t\text{-}Bu_3SiCl$ was used in place of $t\text{-}Bu_3SiI$, there was no detectable reaction in 24 h.

(b) The reaction between I and AgO_2CCF_3 in refluxing CF_3CO_2H was ca. 65% complete after 30 min. After 1 h work-up gave $t\text{-}Bu_3SiO_2CCF_3$ in 87% yield. Under fairly similar conditions the reaction of $TsiSiMe_2I$ (to give $TsiSiMe_2O_2CCF_3$) was complete within 0.5 h, and that of $TsiSiEt_2I$ within 10 min [4] *.

(c) No reaction was observed when $t\text{-}Bu_3SiCl$ was refluxed for 5 h with AgO_2CCF_3

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* When reactions with silver salts are said to be complete within a certain time they were not normally monitored, and may have been complete within a markedly shorter time.

in CF_3CO_2H. Reaction of $TsiSiMe_2Cl$ under comparable conditions was complete within 0.5 h [4].

(d) The reaction of I with $AgOSO_2CF_3$ in refluxing CCl_4 was ca. 15% complete after 12 h and 56% complete after 56 h, and after 75 h work-up gave the triflate $t\text{-}Bu_3SiOSO_2CF_3$, (II), in 85% yield. A similar reaction in refluxing toluene was ca. 20% complete after 8 h, and after 60 h work-up gave II in 90% yield.

In contrast, the triflate $TsiSiMe_2OSO_2CF_3$ was isolated in 85% yield [13] from reaction between $TsiSiMe_2I$ and $AgOSO_2CF_3$ in CH_2Cl_2 for 1 h at room temperature.

(e) No reaction took place between I and freshly prepared AgOCN in Et_2O or CH_2Cl_2 in 48 h at room temperature or under reflux. In contrast, $TsiSiMe_2OCN$ was isolated in 93% yield after reaction of $TsiSiMe_2I$ with AgOCN in CH_2Cl_2 for 1 h, and monitoring of the reaction indicated that it was essentially complete within 15 min [14].

(f) The reaction between I and $AgNO_3$ in refluxing MeOH ('dried', but evidently containing some water or absorbing it during the refluxing) was complete in 7 days, and gave a 60/40 mixture of $t\text{-}Bu_3SiOMe$ and $t\text{-}Bu_3SiOH$. Monitoring indicated that no dectable reaction had occurred after 6 h, and after 42 h (I), $t\text{-}Bu_3SiOMe$, and $t\text{-}Bu_3SiOH$ were present in ca. 55/35/10 ratio.

In contrast, reaction of $TsiSiPh_2I$ with $AgNO_3$ in refluxing MeOH (to give a mixture of $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OMe)$ and $(Me_3Si)_2C(SiPh_2Me)(SiMe_2ONO_2))$ was complete within 10 min, and that of $TsiSiMe_2I$ (to give $TsiSiMe_2OMe$ and $TsiSiMe_2ONO_2$) within 30 min [4].

2. *Solvolysis* *

A. Reactions of t-Bu₃SiI (I)

(a) A solution of I in MeOH (dried by standard methods) was kept in a sealed NMR tube at 60 °C. The ^1H NMR spectrum showed that I and $t\text{-}Bu_3SiOMe$ were present in roughly 98/2 and 96/4 ratio, approximately, after 18 and 30 d, respectively. In contrast the half-life for the methanolysis of $TsiSiMe_2I$ at this temperature would be ca. 7 d (as estimated from data at 50 °C and at the reflux temperature [6,15]). Since by the NMR technique used it is impossible to determine product ratios accurately when one of the components forms less than 10% of the mixture, the data for the reaction of I are subject to large error, but is seems that $TsiSiMe_2I$ must be at least 30 times as reactive as I towards MeOH.

(b) When a solution of I in MeOH containing 2*M* NaOMe was kept at 60 °C, ca. 10% was converted into $t\text{-}Bu_3SiOMe$ in 18 d and ca. 20% in 30 d. The presence of 2 *M* base thus increased the rate of solvolysis, perhaps by a factor of about 5.

When a solution of $TsiSiMe_2I$ was kept under similar conditions the product was $(Me_3Si)_2CHSiMe_2OMe$ (see ref. 16), the approximate ratios of $TsiSiMe_2I/(Me_3Si)_2CHSiMe_2OMe$ at various times being: 75/25, 2 h; 55/45, 4 h; 35/65, 9 h. The reaction of the trisyl compound is evidently much faster than that of I, but since it reacts by fragmentation not substitution no direct comparison is possible. How-

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* Values of rate constants and half lives ($t_{1/2}$) quoted here are only approximate, and meant to be used only for rough internal comparisons within this series of studies.

ever, since the reaction of I with MeOH alone is much slower than that of $TsiSiMe_2I$ (to give the substitution product), and since base has a relatively small effect on the rate of substitution in both reactions, it is safe to conclude that the substitution of I with MeOH containing NaOMe is markedly slower than that of $TsiSiMe_2I$.

(c) The reaction of I with ca. 5 vol.% $H_2O/MeOH$ * at 60 °C gave a good first order plot up to more than 80% reaction, with $t_{1/2}$ ca. 54 h; the product was $t\text{-}Bu_3SiOH$ (but < 5% of $t\text{-}Bu_3SiOMe$ would have escaped detection). A similar reaction but in the presence of 0.1 *M* NaOH (a large excess over the iodide) also gave good first order kinetics with $t_{1/2}$ ca. 48 h. Thus, as in the methanolysis (in absence of water) of $TsiSiMe_2X$ with $X = I$, $OClO_3$ [5], or OSO_2CF_3 [13], the presence of 0.1 *M* base causes only a very small acceleration.

For direct comparison the reaction of $TsiSiMe_2I$ in 5 vol.% $H_2O/MeOH$ containing 0.1 *M* NaOH was examined. A good first order plot was obtained for the disappearance of the iodide, with $t_{1/2}$ ca. 68 h (the product being $TsiSiMe_2OH$). The reactivities of I and $TsiSiMe_2I$ are thus fairly similar under these conditions, with the former about 1.4 times the more reactive.

(d) Hydrolysis of I in (i) 2 vol.% and (ii) 5 vol.% $H_2O/MeCN$ at 62 °C gave satisfactory first order plots with approximate $t_{1/2}$ values of 29 and 14 h. The half-life for the hydrolysis of $TsiSiMe_2I$ in 2 vol.% $H_2O/MeCN$ at 62 °C was ca. 42 h, suggesting that I is about 1.4 times as reactive as $TsiSiMe_2I$ under these conditions.

(e) Hydrolysis of I at 60 °C in 2 vol.% H_2O/Me_2SO, (i) alone and (ii) in the presence of 0.10 *M* NaOH gave first order plots, with $t_{1/2}$ ca. 63 min in both cases.

In 2 vol.% H_2O/Me_2SO at 60 °C, $TsiSiMe_2I$ gave a satisfactory first order plot with $t_{1/2}$ ca. 12 min. Thus this iodide is ca. 5 times as reactive as I under these conditions.

(f) Hydrolysis of I at 70 °C in 5 vol.% H_2O/Me_2SO had $t_{1/2}$ ca. 50 min. Hydrolysis of $t\text{-}Bu_3SiCl$ under identical conditions was only 25% complete after 190 min, indicating that the chloride is ca. 9 times less reactive than the iodide under these conditions.

(g) When a solution of I in 2 vol.% H_2O/DMF was kept at 60 °C, a satisfactory first order plot was obtained with $t_{1/2}$ ca. 80 min.

(h) When a solution of I in 2 vol.% $H_2O/dioxane$ was kept at 60 °C, $t_{1/2}$ was ca. 30 d.

(i) When a solution of I in CF_3CO_2H (which had been dried over P_2O_5) was refluxed, after 13 d ca. 98% of the starting material remained. After 20 d 86% remained, and 8% of $t\text{-}Bu_3SiOH$ and 6% of $t\text{-}Bu_3SiO_2CCF_3$ had been formed; after 31 d the corresponding proportions were 24, 30, and 46%. The reaction apparently speeded up after an initial slow period, possibly because of absorption of water from the atmosphere. There is no doubt, however, that the reaction of I with CF_3CO_2H alone is much slower (probably by a factor of at least 500) than that of $TsiSiMe_2I$, which was ca. 46% complete after 18 h under reflux (the product being exclusively $TsiSiMe_2O_2CCF_3$); it is also much slower than that of $TsiSiEt_2I$, which was complete after 7 d under reflux [4].

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* For the exact composition of the mixed solvent in this and other cases see the Experimental section.

B. Reactions of $t\text{-}Bu_3SiOSO_2CF_3$ (II)

(a) The reaction of II in (dried) MeOH (to give $t\text{-}Bu_3SiOMe$) at 35 °C gave a satisfactory first order plot, with k 1.7×10^{-2} min^{-1} ($t_{1/2}$ ca. 41 min). The reaction is thus fairly similar in rate to that of $TsiSiMe_2OSO_2CF_3$, which has a half-life of ca. 50 min under similar conditions [13].

(b) Attempts to determine the effect on the rate of the methanolysis of the presence of base or LiCl were complicated by the presence of some water, presumably absorbed during the making up of the solutions. Thus the first order plot for the disappearance of II in 0.1 *M* NaOMe/MeOH at 35 °C showed a steeper initial portion (up to about 25% reaction) with a slope corresponding to k ca. 3.0×10^{-2} min^{-1}, during which the $t\text{-}Bu_3SiOH/t\text{-}Bu_3SiOMe$ ratio was > 1, then a curve-off, during which the value of the ratio fell, and a final linear portion (from 55–85% reaction) with a slope corresponding to k ca. 1.6×10^{-2} min^{-1}; the final value of the ratio was 32/68. The value of k for the later stages of the reaction, after much of the water had been consumed, was fairly close to that observed in MeOH in absence of base.

Similarly, with 0.2 *M* NaOMe, there was an initial slope corresponding to k ca. 2.8×10^{-2} and a later slope corresponding to k ca. $1.6\text{–}10^{-2}$. Up to 20% completion of reaction the $t\text{-}Bu_3SiOH/t\text{-}Bu_3SiOMe$ ratio was > 1, but the final ratio was again ca. 32/68.

With 0.2 *M* LiCl in MeOH the inital slope corresponded to k ca. 2.8×10^{-2} min^{-1} and the later slope to k ca. 1.7×10^{-2} min^{-1}. The final $t\text{-}Bu_3SiOH/t\text{-}Bu_3SiOMe$ ratio was virtually identical to that in the presence of 0.1 and 0.2 *M* NaOMe.

The times for disappearance of half of the initial II in presence of 0.1 or 0.2 *M* NaOMe or 0.2 *M* LiCl were ca. 32, 32 and 26 min, respectively, indicating that base has little specific effect on the rate.

(c) The reaction of II in 1 vol.% H_2O/MeOH at 35 °C gave a good first order plot with k 2.4×10^{-1} min^{-1} ($t_{1/2}$ ca. 2.8 min). The same value of k was obtained in the presence of 0.10 *M* NaOH. The reactions were ca. 14 times as fast as that with MeOH alone. The product was $t\text{-}Bu_3SiOH$.

In 2 vol.% H_2O/MeOH, the value of k was 0.71 min^{-1} in the absence and in the presence of 0.10 *M* NaOH. Superficially, comparison of k values suggest that the rate in 2% H_2O/MeOH is ca. 3 times that in 1% H_2O/MeOH, whereas a factor of ca. 2 might be expected, but the rate in 2% H_2O/MeOH ($t_{1/2}$ ca. 1 min) is too fast for reliance to be placed on the absolute value of k, though the similarity of the rates in presence and absence of base is not in doubt.

(d) When a solution of II in CF_3CH_2OH was kept at 60 °C, ca. 30% of II had disappeared after 3 d, to give exclusively $t\text{-}Bu_3SiOH$, some water evidently being present.

C. Reactions of $t\text{-}Bu_3SiI$ and $t\text{-}Bu_3SiCl$ with alkali metal salts

1. Reactions in MeOH. (a) When a solution of I (0.015 *M*) and NaN_3 (0.10 *M*) in MeOH was refluxed an approximate first order plot was obtained for conversion of I into $t\text{-}Bu_3SiN_3$ up to about 80% reaction, with $t_{1/2}$ ca. 45 h.

For reaction of $TsiSiMe_2I$ under similar (pseudo first order) conditions $t_{1/2}$ was ca. 11 h at 60 °C [15], indicating that this iodide is roughly 6 times as reactive as I (after allowance for the temperature difference).

(b) When a solution of I (0.015 *M*) and KSCN (0.10 *M*) in MeOH was refluxed, conversion of I into t-Bu_3SiNCS was half-complete in ca. 52 h.

Under similar conditions ca. 62% of $TsiSiMe_2I$ reacted in 24 h (to give $TsiSiMe_2NCS$ and $TsiSiMe_2OMe$ in ca. 4/1 ratio) [15], suggesting that this iodide is roughly 3 times as reactive as I towards KSCN in this medium.

(c) When a solution of I (0.015 *M*) and CsF (0.10 *M*) in MeOH was refluxed, half of the I disappeared in ca. 130 h, to give t-Bu_3SiF and t-Bu_3SiOMe in ca. 55/45 ratio.

Under similar conditions ca. 90% of $TsiSiMe_2I$ reacted in 24 h to give $TsiSiMe_2F$ and $TsiSiMe_2OMe$ in ca. 8/1 ratio [15], suggesting that this iodide may be as much as 30 times as reactive as I towards CsF in this medium, but this figure is subject to a very large degree of uncertainty.

2. Reactions in MeCN. (a) When a solution of I (0.54 mmol) in MeCN (15 cm^3) was refluxed in the presence of NaN_3 (3.2 mmol), about 80% conversion into t-Bu_3SiN_3 took place in 15 h, and the reaction was virtually complete after 30 h.

Under similar conditons the conversion of the chloride t-Bu_3SiCl into t-Bu_3SiN_3 was complete in 15 h, showing that the chloride is somewhat more reactive than the iodide in this system.

(b) When a solution of I (0.015 *M*) and KSCN (0.20 *M*) in MeCN was kept at 60 °C satisfactory (pseudo) first order kinetics were observed for conversion of I into t-Bu_3SiNCS with $t_{1/2}$ 66 min.

Under similar conditions the reaction of t-Bu_3SiCl had $t_{1/2}$ 10 min, and that of $TsiSiMe_2I$ had $t_{1/2}$ 32 min. Thus t-Bu_3SiCl is ca. 7 times as reactive as t-Bu_3SiI under these conditions, and the latter ca. half as reactive as $TsiSiMe_2I$.

(c) When KOCN was used in place of KSCN in the procedure described in (b) above, the values of $t_{1/2}$ for I and t-Bu_3SiCl were ca. 27 and 5 h, respectively. Thus the chloride is ca. 5 times as reactive as the iodide under these conditions.

The reaction of $TsiSiMe_2I$ with 0.10 *M* KOCN was previously shown to be ca. 60% complete in 6 h at the boiling point (82°C). Allowing for the different salt concentration, and roughly estimating the rate decrease on going from 82 to 60 °C as 5–10, we conclude that this iodide is ca. 1.2–2.5 times as reactive as t-Bu_3SiI.

Discussion

1. Reactions with silver salts

The reactions of I with silver salts are evidently much slower than those of $TsiSiMe_2I$ and even $TsiSiPh_2I$. The reaction of I with $AgNO_3$ in MeOH did not give any detectable amount of t-Bu_3SiONO_2 (whereas $TsiSiMe_2I$ gave a mixture of the corresponding methoxide and nitrate), but it is possible that some nitrate was formed but then solvolysed during the prolonged refluxing.

The chloride t-Bu_3SiCl is much less reactive than the iodide towards AgO_2CCF_3 in CF_3COOH, and it is probable that the reactivity ratio t-Bu_3SiI/t-Bu_3SiCl is substantially greater than the corresponding $TsiSiMe_2I/TsiSiMe_2Cl$ ratio under such conditions.

We cannot be sure that the reactions of t-Bu_3SiI with silver salts involve silicocationic intermediates, as do those of $TsiSiR_2I$ compounds, but it is quite likely that they do, and that the higher rate of reaction for the trisyl compounds is at least partly attributable to the stabilization of the forming cation by methyl-bridging, as in **A**.

2. *Solvolysis*

The solvolysis of t-Bu_3SiI and t-$Bu_3SiOSO_2CF_3$ in MeOH, H_2O/MeOH, and H_2O/Me_2SO are little, if at all, accelerated by the presence of base in low concentrations (e.g. 0.1 *M*); the absence of acceleration by NaOH in H_2O/Me_2SO is especially significant, since hydroxide ion is powerfully nucleophilic towards silicon under these conditions, as shown by the rapid cleavage of Si–C bonds in such media [19]. This observation indicates that, as for the $TsiSiMe_2X$ species [20], the solvolyses are not of the simple S_N2 type, and may well have the S_N2-intermediate mechanism [21] in which there is nucleophilic participation by the solvent in the rate-determining transition state, though also much ionic character arising from incipient breaking of the Si–X bond [20]. Such ionic character is consistent with the observation that the chloride t-Bu_3SiCl is ca. 9 times less reactive than the iodide in hydrolysis by 5 vol.% H_2O/Me_2SO whereas the chloride is the more reactive in S_N2 reactions with alkali metal salts.

In an S_N2-intermediate process, nucleophilic participation by the solvent may reduce or replace the methyl-bridging which is thought to facilitate ionization of $TsiSiMe_2I$, and in keeping with this the differences in reactivity between this iodide and t-Bu_3SiI are relatively small in methanolysis and hydrolysis, varying from a factor of > 30 in the reaction with MeOH alone to ca. 5 in 2 vol.% H_2O/Me_2SO, and 0.7 in 5 vol.% H_2O/MeOH and 2 vol.% H_2O/MeCN. If as we suspect (see the discussion of the reactions with salts, below) steric crowding is usually somewhat greater for approach of a nucleophile to t-Bu_3SiI than to $TsiSiMe_2I$, then it is not surprising that the rate of reaction increases more in the case of t-Bu_3SiI on changing from MeOH as nucleophile to the less bulky H_2O. We cannot at present, however, explain why, when t-Bu_3SiI is less reactive than $TsiSiMe_2I$ in both S_N1 and S_N2 mechanisms, the order of reactivity should apparently be reversed for hydrolysis in some media, in a process which is thought to have some of the character of both those mechanisms.

The similarity of the rates of reaction of t-$Bu_3SiOSO_2CF_3$ and $TsiSiMe_2OSO_2CF_3$ with MeOH was initially surprising, but the change from iodide to the better leaving group triflate could well accelerate an S_N2-intermediate type of process more effectively for the more crowded transition states with t-Bu_3SiX than the somewhat less crowded transition states with $TsiSiMe_2X$ systems. The reaction of the triflate is accelerated much more than that of the iodide by the presence of water; similar sensitivity towards the presence of water is shown by the trisyl compounds $TsiSiMe_2X$ where X = OSO_2CF_3 [13], $OClO_3$ [5], or OCN [22].

The triflate (II) reacts only very slowly (if at all) with CF_3CH_2OH. Similar observations were made with $TsiSiMe_2OSO_2CF_3$ [13], and with $TsiSiMe_2OClO_3$ [5], and the behaviour can be attributed to the fact that while this alcohol is a much better ionizing solvent that MeOH it is also much less nucleophilic [21], and this latter factor dominates in an S_N2-intermediated type of process [20].

Especially significant is the fact that the reaction of t-Bu_3SiI with CF_3CO_2H is much slower (probably by a factor of at least 500) than that of $TsiSiMe_2I$, since the solvolysis of the latter in this medium is thought to involve rate-determining formation of a silico-cation [4], and this is evidently a much less favourable process for t-Bu_3SiX than for $TsiSiMe_2X$ species, as revealed by the relative reactivities towards silver salts.

In the hydrolysis of t-Bu_3SiI, water was found to be much more active in Me_2SO or DMF than in MeCN or dioxane. This observation could be of value in preparative procedures in these highly sterically hindered systems.

3. Reactions with alkali metal salts

We first note some minor features of interest in these reactions: (a) In MeOH, NaN_3 is more reactive than KSCN towards t-Bu_3SiI, as towards $TsiSiMe_2I$ [15], but CsF appears to be less reactive than KSCN towards the former iodide whereas the opposite is the case towards the latter iodide. In MeCN the sequence of reactivity towards t-Bu_3SiI, viz. KSCN > KOCN > CsF, is the same as that towards $TsiSiMe_2I$ [15].

(b)The reactions of t-Bu_3SiI with the salts are generally slower than those of $TsiSiMe_2I$, the factor between them usually being in the range of 3–8. (Preliminary work suggests that t-Bu_3SiI and $TsiSiPh_2I$ may have roughly comparable reactivities in this type of reaction [17].)

The most surprising observation from the work on the reactions of t-Bu_3SiX species with alkali metal salts is that in the cases examined, viz. the reactions with NaN_3, KSCN or KOCN in MeCN, the chloride reacted more readily than the iodide, the factor between them being ca. 6 for reactions with KOCN and KSCN. In the case of the trisyl compounds, $TsiSiMe_2X$, the iodide is more reactive than the chloride, but the difference in reactivity is fairly small, involving a factor of roughly 6 [18], whereas an iodide would normally be expected to be much more reactive than a chloride (as in S_N2 substitutions involving alkyl halides).

It is not difficult to envisage a situation in which a silicon chloride could be more reactive than the corresponding iodide in a bimolecular substitution process involving attack by Y^-. If the rate-determining transition state is close in structure to that of the (possibly hypothetical) intermediate $[R_3SiXY]^-$, then it seems quite possible that in a very crowded system the bulk of the iodine atom would make the energy of the transition state higher for $X = I$ than for $X = Cl$, this (reinforced by the greater stabilization of the negative charge on silicon by Cl than by I) outweighing the greater ease of stretching the Si–I than the Si–Cl bond. (In contrast, in reactions of such sterically hindered silicon halides in solvolysis or reactions with silver salts, in which nucleophilic attack is absent or less important, the much greater ease of stretching of the Si–I bond would be the greatly dominant factor.)

The above discussion raises once again the question of whether nucleophilic substitutions at silicon in ordinary R_3SiX species (where R is a not especially bulky alkyl or aryl group) the reactions proceed through a 5-coordinate intermediate. If they do, then for $X = Cl$ and I we can assume that in reactions with powerful nucleophiles Y^- such as OH^-, OMe^-, N_3^-, F^-, NCO^- etc., the departure of X^- from the intermediate would be faster than that of Y^-, and thus that the rate-determining step would be the formation of the intermediate. In this case one would rather expect the energy of the (rate-determining) transition state (and that of the intermediate) to be lower for $X = Cl$ than for $X = I$ because of the greater stabilization of the negative charge by the more electronegative Cl than the less electronegative I ligand (as in many nucleophilic aromatic substitutions involving displacement of halogens in which the formation of the carbanionic intermediate is rate-determining). It is conceivable that the greater ease of stretching the Si–I than the Si–Cl bond on going to the 5-coordinate intermediate would compensate for this, but it is difficult to imagine that the iodides would be much more reactive than the chlorides, as they are normally assumed to be. (There is, in fact, as far as we are aware no direct evidence that organosilicon iodides are generally far more reactive than chlorides towards nucleophilic anions, but it would by surprising if they proved not to be.) If the reaction path avoids an actual 5-coordinate intermediate, so that significant stretching of the Si–X bond is synchronous with the formation of the Si–Y bond, then, of course, the iodides would be expected to be much more reactive than the chlorides (again as in S_N2 substitutions in alkyl halides).

Conclusion

The following tentative generalizations can be drawn from the above discussion:

(a) Under conditions in which $TsiSiMe_2I$ is thought to react through a silico-cationic intermediate, in which methyl-bridging as in **A** may provide anchimeric assistance, namely in reactions with silver salts and in solvolysis in CF_3CO_2H, this iodide is much more reactive than t-Bu_3SiI.

(b) Under conditions involving S_N2 processes, such as in the reactions with alkali metal salts, $TsiSiMe_2I$ is generally more reactive than t-Bu_3SiI (steric hindrance to formation of a 5-coordinate transition state apparently being greater for the latter) but the difference between the two iodides is much smaller than in the reactions mentioned under (a) above.

(c) In solvolysis under conditions in which an S_N2-intermediate mechanism may operate, in which the ease of ionization of the Si–X bond is less dominant than in S_N1 processes, the differences in reactivity between $TsiSiMe_2X$ and t-Bu_3SiX compounds are again fairly small (with the trisyl compounds usually the more reactive). The difference in reactivity between $TsiSiMe_2I$ and t-Bu_3SiI is substantially smaller in hydrolysis than in methanolysis, reflecting the greater crowding in the case of t-Bu_3SiI.

(d) The differences between the reactivities of corresponding chlorides and iodides in these highly hindered systems are smaller in reactions in which participation by the nucleophile is important than in those in which the ease of ionization of the Si–X is dominant. When the hindrance is very large, as in the reactions of t-Bu_3SiX species with anions, the chloride can be significantly more reactive than the iodide.

Experimental

Materials

The compounds t-Bu_3SiH, t-Bu_3SiI [10a] and $TsiSiMe_2I$ [3] were made by published methods. The chloride t-Bu_3SiCl was made by treating the hydride with ICl (not with Cl_2 as previously used [10a]). Thus a mixture of t-Bu_3SiH (5.6 mmol) and ICl (28 mmol) in CCl_4 (40 cm^3) was stirred at room temperature for 3 h; the solution was washed with aqueous $NaHSO_3$ to remove the excess of ICl, then dried ($MgSO_4$) and evaporated, and the residue was sublimed (100 °C/0.01 mmHg) to give t-Bu_3SiCl (85%), m.p. 117–118 °C (lit. 10a, 116–118 °C).

Methanol was dried by refluxing with and distillation from $Mg(OMe)_2$, and stored over Molecular Sieve 3A. Acetonitrile was dried similarly with P_2O_5 and stored over Molecular Sieve 4A. 2,2,2-Trifluoroethanol was dried similarly with CaH_2, and stored over Molecular Sieve 4A.

All salts were dried by standard methods.

NMR spectra

The ^1H NMR spectra were normally recorded with solutions in CCl_4 containing 5% CH_2Cl_2 as lock and reference. The chemical shifts observed for the t-Bu_3SiX species are listed in Table 1. All shifts are in ppm.

For monitoring reactions in MeOH or CF_3CH_2OH, the spectra of the alcoholic solutions were recorded using the CH_3 or CH_2 protons as lock and reference.

Reactions with silver salts

(a) A solution of I (0.26 g, 0.67 mmol) and AgO_2CCH_3 (0.16 g, 1 mmol) in anhydrous CH_3CO_2H (15 cm^3) was refluxed. Small samples were removed at intervals, and added to hexane; the mixture was shaken with water, the hexane layer was well washed then evaporated, the residue was taken up in CCl_4 and the ^1H NMR spectrum was recorded. This procedure showed that reaction was ca. 50% complete after 2 h and ca. 85% after 5 h. After 8 h hexane was added to the main reaction mixture, and the solution was decanted from the AgI and added to water. The organic layer was washed several times with water, dried ($MgSO_4$), and evaporated to leave a solid, which was sublimed (80 °C/0.05 mmHg) to give t-$Bu_3SiO_2CCH_3$ (0.17 g, 82%), m.p. 73°C; ν(CO) 1730, 1250 cm^{-1}; δ 1.01 (s, Me_3C) and 1.91 (s, CH_3CO_2); m/z 201 ($[M-Bu]^+$) (Found: C, 65.3; H, 11.9. $C_{14}H_{30}O_2Si$ calcd.: C, 64.9; H, 11.6%).

(b) A solution of t-Bu_3SiCl (0.05 g, 0.30 mmol) in CH_3CO_2H (5 cm^3) was refluxed for 24 h. Work-up as in (a), but without sublimation, gave only unchanged t-Bu_3SiCl (as shown by the ^1H NMR spectrum and GLC).

(c) A solution of I (0.38 g, 1.17 mmol) and AgO_2CCF_3 (0.40 g, 1.81 mmol) in CF_3CO_2H (15 cm^3) was refluxed. Monitoring as in (a) above showed that reaction was ca. 65% complete in 0.5 h. After 1 h work up as in (a) (sublimation at 140 °C/0.1 mmHg) gave t-$Bu_3SiO_2CCF_3$ (0.31 g, 87%), m.p. 51°C; ν (CO) 1770, 1220 cm^{-1}; δ 1.06; m/z 255 ($[M-Bu]^+$) (Found: C, 53.3; H, 8.9. $C_{14}H_{27}O_2F_3Si$ calcd.: C, 53.7; H, 8.6%).

TABLE 1

^1H NMR SPECTRAL DATA FOR t-Bu_3SiX COMPOUNDS[a]

X	δ (ppm) for t-Bu	X	δ (ppm) for t-Bu
F	1.10	$OCOCH_3$[e]	1.01
Cl	1.15	$OCOCF_3$	1.06
I	1.24	OSO_2CF_3	1.22
OH[b]	1.12	NCS	1.10
OMe[c]	1.14	NCO	1.04
OCH_2CF_3[d]	1.20	N_3	1.06

[a] In CCl_4 unless otherwise stated. [b] Broad singlet at δ 4.8 (OH). [c] Singlet at δ 3.40 (OMe). [d] In solution in CF_3CH_2OH, with instrument locked on CH_2 protons of solvent at δ 3.88. [e] Singlet at δ 1.91 ($OCOCH_3$).

(d) Only unchanged t-Bu_3SiCl (^1H NMR and GLC) was recovered when a solution of this chloride (0.060 g, 0.28 mmol) and AgO_2CCF_3 (0.13 g, 0.59 mmol) in CF_3CO_2H (10 cm^3) was refluxed for 5 h.

(e) Monitoring (^1H NMR) of the reaction between I (0.11 g, 0.37 mmol) and $AgOSO_2CF_3$ (0.14 g, 0.55 mmol) in CCl_4 (15 cm^3) showed that reaction was about 15% complete after 12 h, and ca. 80% after 56 h. After 75 h, work-up as in (a) gave t-$Bu_3SiOSO_2CF_3$ (0.10 g, 85%), m.p. 48°C; $\nu(SO_3)$ 1475, 1240 cm^{-1}; δ 1.22; m/z 291 ($[M-Bu]^+$) (Found: C, 44.9; H, 8.1. $C_{13}H_{27}O_3SSiF_3$ calcd.: C, 44.7; H, 7.7%).

(f) A solution of I (0.090 g, 0.30 mmol) and $AgOSO_2CF_3$ (0.11 g, 0.44 mmol) in toluene (10 cm^3) was refluxed. After 8 h the reaction was ca. 20% complete. After 60 h, work-up as in (a) gave t-$Bu_3SiOSO_2CF_3$ (90%).

(g) No reaction took place when a mixture of I (0.38 mmol) and (freshly prepared) AgOCN (0.43 mmol) in CH_2Cl_2 (10 cm^3) was refluxed for 48 h. A similar result was obtained using Et_2O as solvent.

(h) A solution of I (1.33 mmol) and $AgNO_3$ (1.81 mmol) in MeOH (20 cm^3) was refluxed under N_2. After 6 h no detectable reaction had occurred; after 42 h I, t-Bu_3SiOMe and t-Bu_3SiOH were present (as indicated by ^1H NMR spectroscopy) in roughly 55/30/10 ratio, and the corresponding ratios after 68 and 92 h respectively were 20/50/30 and 15/55/30. After 7 d the usual work-up (but without sublimation) left a mixture of t-Bu_3SiOMe (60%) and t-Bu_3SiOH (40%), as indicated by the ^1H NMR spectrum. The components were separated by TLC (silica gel, light petroleum b.p. 60–80 °C) and their identities confirmed by mass spectrometry.

Solvolysis

A solution described as containing x vol.% of water actually consisted of a mixture of x vol. of water with 100 vol. of solvent.

Reactions involving t-Bu_3SiI (I) or t-Bu_3SiCl. In the reactions involving I, about 0.1–0.3 g of I was usually used in 10–20 cm^3 of solvent. However, for the reactions in anhydrous MeOH ca. 0.02 g was used in 0.5 cm^3 of the solvent.

Reactions with anhydrous MeOH were carried out in a sealed NMR tube, which was kept at the appropriate temperature and removed at intervals for recording of the ^1H NMR spectrum. For reactions in other media, where these were monitored small samples were removed at appropriate times. For reactions in CF_3CO_2H or H_2O/MeOH, ^1H NMR spectra were recorded directly. For reactions in MeCN the solvent was taken off rapidly under vacuum at room temperature, and the residue was dissolved in CCl_4 containing 5% CH_2Cl_2. For runs in H_2O/Me_2SO, H_2O/DMF, or H_2O/dioxane the samples were shaken with a mixture of CCl_4 and H_2O, and the CCl_4 layer was washed with additional water before the spectrum was recorded.

For reactions of I and t-Bu_3SiCl in 5 vol.% H_2O/Me_2SO, reactions were monitored in situ by recording of the ^1H NMR spectrum using the Me_2SO signal as lock.

Reactions of t-$Bu_3SiOSO_2CF_3$ (II). For the reactions with MeOH or H_2O/MeOH, ca. 0.015 g of II was dissolved in a small drop (ca. 7×10^{-3} cm^3) of CH_2Cl_2 in an NMR tube and 0.5 cm^3 of the reaction medium, preheated to 35 °C, was added. The tube was quickly sealed, shaken, and placed in the probe of the NMR spectrometer at 35 °C, and recording of the spectrum was begun.

For the reaction in CF_3CH_2OH, a solution of II (0.15 mmol) in CF_3CH_2OH (15 cm^3) in an NMR tube was initially kept at ca. 21°C for 10 d, and ^1H NMR spectroscopy indicated that ca. 6% of II had been converted into a single product. The solution was then kept at 60 °C for 3 days, after which 30% of II had reacted. Examination by GLC/MS showed that the product was t-Bu_3SiOH.

For comparison, t-$Bu_3SiOCH_2CF_3$ was produced by refluxing a solution of I (0.15 mmol) with $AgClO_4$ (1 mmol) in 'dried' CF_3CH_2OH (15 cm^3) for 72 h. After this time the ^1H NMR spectrum of the solution (with the instrument locked at δ 3.88 on the CH_2 signal of the solvent) showed two components to be present (δ 1.20 and 1.12) in ca. 60/40 ratio. These were identified by GLC/MS as t-$Bu_3SiOCH_2CF_3$ (m/z 241 ($[M - Bu]^+$) and t-Bu_3SiOH, respectively.

Reactions with alkali metal salts. These reactions were monitored by ^1H NMR spectroscopy. For reactions in MeOH the spectra of samples of the solution were recorded directly. For reactions in MeCN, 0.5 cm^3 samples were removed and added to CCl_4 (2 cm^3). The CCl_4 layer was washed several times with water, then evaporated, and the residue was taken up in CCl_4 (0.5 cm^3) containing 5% of CH_2Cl_2 for recording of the ^1H NMR spectrum.

(a) (i) A solution of I (0.50 mmol) and NaN_3 (3.0 mmol) in MeOH (15 cm^3) was refluxed for 7 d, then worked up as described for the preparation of t-$Bu_3SiO_2CCH_3$ (sublimation at 110 °C/0.05 mmHg) to give t-Bu_3SiN_3 (80%), m.p. 112 °C (lit. 10b, 130 °C; [11], 114–116 °C); δ 1.06; $\nu(N_3)$ 2140, 1330 cm^{-1}; m/z 184 ($[M - Bu]^+$) 142 ($[M - Bu - C_3H_6]^+$) (Found: C, 59.8; H, 10.4. $C_{12}H_{27}SiN_3$ calcd.: C, 59.5; H, 11.1%).

(ii) A solution of I (0.15 mmol) and NaN_3 (1 mmol; i.e. 0.10 M) in MeOH (10 cm^3) was refluxed gently under dry N_2 and samples were withdrawn at appropriate intervals and their ^1H NMR spectra recorded; the percentages of reaction at various times were: 16%, 15 h; 38%, 27 h; 51%, 39 h; 62%, 63 h; 60%, 75 h; 74%, 84 h.

(b) (i) In a procedure similar to that described under (a)(i) but using KSCN in place of NaN_3, after 12 h work-up (sublimation at 100 °C/0.01 mmHg) gave t-Bu_3SiNCS (85%), m.p. 61°C (lit. 10b 165–168 °C); δ 1.10; ν(NCS) 2060, 820 cm^{-1}; m/z 200 ($[M - Bu]^+$), 158 ($[M - Bu - C_3H_6]^+$) (Found: C, 60.9; H, 11.0; N, 5.7. $C_{13}H_{27}SiNS$ calcd.: C, 60.6; H, 10.5; N, 5.4%).

(ii) In a procedure similar to that described under (a)(ii), but with KSCN in place of NaN_3, the extents of reactions at various times were: 13%, 15 h; 27%, 27 h; 40%, 39 h; 50%, 51 h; 57%, 62 h; 66%, 72 h; 76%, 87 h.

(c) In a procedure similar to that under (a)(ii), but with CsF in place of NaN_3, the percentages of I which had disappeared after various times were: 3%, 15 h; 10%, 27 h; 15%, 39 h; 29%, 51 h; 38%, 75 h; 56%, 158 h. Both t-Bu_3SiF and t-Bu_3SiOMe were produced, in an average ratio of about 1.3/1 (though possibly as high as 1.5/1 in the early stages).

(d) (i) A solution of I (0.40 mmol) and KOCN (2.6 mmol) in MeCN was refluxed for 5 d. The usual work-up (sublimation at 125 °C/0.01 mmHg) gave t-Bu_3SiNCO (80%); m.p. 113°C (lit. 10b, m.p. 136 °C); ν(NCO) 2270, 1480 cm^{-1}; δ 1.04; m/z 184 ($[M - Bu]^+$), 142 ($[M - Bu - C_3H_6]^+$) (Found: C, 65.0; H, 11.5; N, 5.5. $C_{13}H_{27}SiNO$ calcd.: C, 64.7; H, 11.2; N, 5.8%).

(ii) A solution of I (0.15 mmol) and KOCN (1.0 mmol; i.e. 0.20 M) in MeCN (10 cm^3) was kept at 60 °C and samples were withdrawn at intervals. A good first order plot was obtained with $t_{1/2}$ ca. 27 h.

When t-Bu_3SiCl was used in a similar procedure $t_{1/2}$ was ca. 5 h.

(e) (i) A solution of I (0.16 mmol) and KSCN (10 mmol) in MeCN (10 cm^3) was refluxed for 120 h. The usual work-up gave exclusively t-Bu_3SiNCS, with properties identical to those described under (b) (i).

A similar procedure but with t-Bu_3SiCl in place of I, and with reaction for 90 h, gave exclusively t-Bu_3SiNCS.

(ii) A solution of I (0.15 mmol) and KSCN (2.0 mmol) in MeCN (10 cm^3) was kept at 60 °C, and samples were withdrawn at intervals. A good first order plot was obtained with $t_{1/2}$ 66 min.

When t-Bu_3SiCl was used in a similar procedure $t_{1/2}$ was 10 min.

(f) A mixture of I (0.54 mmol) and NaN_3, (3.2 mmol) in MeOH (15 cm^3) was refluxed. Removal of a sample after 15 h and analysis by GLC (5% OV 101 on Chromosorb B) showed that conversion into t-Bu_3SiN_3 was ca. 80% complete. After 27 h the usual work-up (sublimation at 100 °C/0.05 mmHg) gave t-Bu_3SiN_3 (90%).

When t-Bu_3SiCl was used in place of I, reaction was found to be complete after 15 h.

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