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Effects of the substituents Y in reactions of compounds of the type $(Me_3Si)_3CSiH(C_6H_4Y\text{-}p)I$. Evidence against the S_N2(intermediate) mechanism for methanolysis of $(Me_3Si)_3CSiMe_2I$ and $(Me_3Si)_3CSiHPhI$

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Abstract

The rates of methanolysis of the iodides $TsiSiH(C_6H_4Y\text{-}p)I$ (Y = MeO, Me, H, Cl, or CF_3) in 1/1 v/v MeOH/dioxane have been shown to be increased by electron withdrawal by Y and correspondingly decreased by electron release. This is taken to imply that the methanol is covalently involved in the transition state, and thus that, contrary to an earlier suggestion, the reaction cannot have an S_N2(intermediate) mechanism. No explanation can at present be offered for the fact that methanolysis of TsiSiHPhI (like that of $TsiSiMe_2X$ with X = I, $OClO_3$, or OSO_2CF_3) is not accelerated by NaOMe whereas that of some other TsiSiHPhX compounds (e.g. X = Br, ONO_2, or OSO_2Me) is so accelerated, with its implications of a duality of mechanism within an S_N2 range. The reactions of the iodides $TsiSiH(C_6H_4Y\text{-}p)I$ with KSCN in MeCN are also accelerated by electron withdrawal by Y, whereas those with AgOAc in $MeCO_2H$ are accelerated by electron release.

Introduction

The severe steric hindrance to direct nucleophilic attack at functional silicon centres bearing the bulky 'trisyl' group, $(Me_3Si)_3C$, denoted here by Tsi, or a related group, has allowed observations of previously inaccessible mechanisms of reaction at such centres [1]. In particular the reactions of $TsiSiR_2I$ species with electrophiles, viz. Ag^I or Hg^{II} salts [2], ICl [3] CF_3CO_2H [2], *m*-chloroperoxybenzoic acid in MeOH [4], or with MeOH under UV irradiation [5], all give rearranged products $(Me_3Si)_2C(SiR_2Me)(SiMe_2Z)$, either exclusively or along with the unrearranged products $TsiSiR_2Z$; e.g. reaction of $TsiSiPh_2I$ with silver salts AgZ gives exclusively the rearranged product $(Me_3Si)_2C(SiPh_2Me)(SiMe_2Z)$ [2]. There is strong evidence that these reactions involve rate-determining formation of a bridged cation of type I

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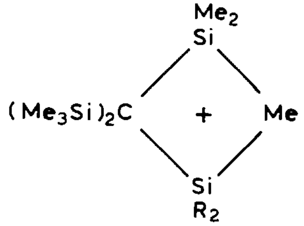
(the migrating γ-Me group thus providing anchimeric assistance), which is then attacked by a nucleophile Z^-, with opening of the four-membered ring, at either the α- or γ-Si atom, attack at the least hindered centre normally being favoured.



(I, R = Et)

The solvolysis of $TsiSiEt_2I$ (and by implication that of $TsiSiMe_2I$) in the strongly electrophilic solvent CF_3CO_2H also results in such rearrangement, and thus can be assumed to involve rate-determining ionization to give a cation of the type I (R = Et); the rate of reaction is not significantly affected by addition of NaO_2CCF_3 [2]. The methanolysis of the compounds of the type $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$ [6] and $(Me_3Si)_2C(SiMe_2CH{=}CH_2)(SiMe_2I)$ [7], in which the γ-OMe and (to a lesser extent) the γ-$CH{=}CH_2$ group provide powerful anchimeric assistance, also involve rate-determining ionization (and thus, by definition, are S_N1 processes, although the rate-determining step actually involves intramolecular nucleophilic attack on the α-Si by the migrating group); thus the rates of the reactions are little changed by the presence of NaOMe, and the reactions are markedly faster in the more electrophilic but less nucleophilic solvent CF_3CH_2OH.

At the other end of the mechanistic spectrum, reactions of $TsiSiMe_2I$ with alkali metal salts (e.g. NaN_3 or KSCN) in MeOH or MeCN appear to be S_N2 nucleophilic displacement processes, involving a five-coordinate intermediate and/or transition state, the reaction being of first-order with respect to both the iodide and the salt [7–9].

The methanolysis of the compounds TsiSiHPhX with e.g. X = Br [10], ONO_2 [10], F [11], or OSO_2Me [11] are strongly accelerated by addition of NaOMe, the rate increase being proportional to the concentration of the base, and thus it is reasonable to assume that the reactions are of the S_N2 type. In contrast, the methanolysis of the iodides TsiSiHPhI and TsiSiHMeI is not significantly affected by the presence of NaOMe [10], and the same was found to be true for the methanolysis of the compounds $TsiSiMe_2X$, with X = I [12], $OClO_3$ [10], or OSO_2CF_3 [13]. (The presence of 0.1 *M* base was also found to have only small effects in solvolysis of $TsiSiMe_2I$ and $t\text{-}Bu_3SiI$ in 5 vol-% H_2O/MeOH and of the latter iodide in 2 vol-% H_2O/Me_2SO [9]). Thus, by the reasoning long-used in connection with nucleophilic displacements at saturated carbon centres, it seemed likely that these reactions were of the S_N1 type. However, doubt was cast on this by the fact that the solvolysis of the iodide TsiSiMeHI and the perchlorate $TsiSiMe_2OClO_3$ was slower in CF_3CH_2OH than in MeOH [10], and later the involvement of cationic intermediates, which would be formed in the S_N1 process, was ruled out by the observation that no rearrangements occurred in solvolysis of $TsiSiR_2I$ species [14].

The seeming conflict of a lower rate of reaction in CF_3CH_2OH than in MeOH combined with absence of rate enhancement by NaOMe has been observed for reactions of some organic halides, e.g. for t-butyl halides, and has led to the proposal that these reactions have an S_N2(intermediate) mechanism, in which there is nucleophilic solvation of the forming cationic centre in the rate-determining transition state, which nevertheless has much carbocationic character and leads to a carbocation (within a nucleophilically solvated ion-pair) that is not necessarily trapped by the solvating nucleophile [15]. (This interpretation has, however, been critized [16].) We thus tentatively suggested that the alcoholysis of TsiSiHPhI and of the $TsiSiMe_2X$ compounds with X = I, $OClO_3$, or OSO_2CF_3, which show some similar characteristics, might also be of the S_N2(intermediate) type, although there was a significant difference in that the transition state for the reactions of the silicon compounds evidently did not lead to a fully-formed cation (even within an ion-pair), since if it did then rearrangements would have been observed with appropriate $TsiSiR_2I$ compounds *.

If the methanolysis of TsiSiHPhI (and hence of the relevant $TsiSiMe_2X$ compounds) were indeed, of the S_N2(intermediate) type, the functional silicon centre would become more positive in the transition state, and thus electron release by Y in the compounds $TsiSiH(C_6H_4Y\text{-}p)I$ would be expected to increase, and electron withdrawal by Y to reduce, the rate, and so we decided to examine the effects of Y in methanolysis for Y = MeO, Me, H, Cl, and CF_3. For comparison we also looked at the approximate effects of substituents in reactions of the $TsiSiH(C_6H_4Y\text{-}p)I$ in the S_N2 reactions with KSCN in MeCN (to give the corresponding $TsiSiH(C_6H_4Y\text{-}p)NCS$ compounds), which would be expected to be facilitated by electron withdrawal by Y, and in the reactions with AgO_2CMe in $MeCO_2H$ (to give the acetates $TsiSiH(C_6H_4Y\text{-}p)(O_2CMe)$, which would be expected to be facilitated by electron release by Y.

Results and discussion

To provide a convenient rate of methanolysis at 35 °C a 1/1 v/v MeOH/dioxane mixture was used. The progress of the reaction was monitored by ^1H NMR spectroscopy, the relative heights of the signals from the Tsi group in the substrate $TsiSiH(C_6H_4Y\text{-}p)I$ and the product $TsiSiH(C_6H_4Y\text{-}p)OMe$ being noted at various times. Good first order kinetics were observed, and the rate constants and derived values, $t_{1/2}$, of the time for half completion of the reaction are listed in Table 1, along with the values of k_{rel}, the rate constant relative to that for the parent compound TsiSiHPhI. It is evident that the reaction is assisted by electron withdrawal by Y and retarded by electron release; a plot of log k_{rel} against σ (Fig. 1) is a good straight line ($r = 0.997$), with a slope, ρ, of 0.73.

The observations indicate that the functional silicon centre becomes more negative in the transition state, and this seems to rule out the S_N2(intermediate) mechanism. They would be consistent with rate-determining formation or decomposition (by loss of I^-) of a five-coordinate intermediate $[TsiSiH(C_6H_4Y\text{-}p)I(OMe)]^-$, or with a concerted but not fully synchronous process in which the formation of the O–Si bond was more advanced in the transition state than the

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* In our view this absence of rearrangement rules out a proposal [16a] that the reaction involves attack of a nucleophile at silicon within an ion-pair.

Table 1

Rate data for reactions of $TsiSiH(C_6H_4Y\text{-}p)I$ compounds with 1/1 v/v MeOH/dioxane at 35 °C

Y	$10^2 k$ (s^{-1}) [a]	$t_{1/2}$ (min)	k_{rel}
MeO	1.43	48.5	0.65
Me	1.52	45.5	0.69
H	2.20	31.5	1.00
Cl	3.30	21	1.50
CF_3	5.30	13	2.42

[a] Observed first-order rate constant.

breaking of the Si–I bond. That is, the process is of the S_N2 type, but with the complication that for attack at silicon, as distinct from that at carbon, the 5-coordinate state could be a real intermediate and not just a transition state. (The fact that towards KSCN in MeCN the iodide $TsiSiMe_2I$ is only a few times as reactive as the chloride $TsiSiMe_2Cl$, and t-Bu_3SiI actually less reactive than the chloride t-Bu_3SiCl, has been taken as evidence in favour of rate-determining formation of five coordinate intermediate in that reaction [9].) *

Rate data obtained (by similar monitoring by ^1H NMR spectroscopy) for the reactions of the $TsiSiH(C_6H_4Y\text{-}p)I$ compounds with KSCN in MeCN were rather imprecise because the reactions were so fast, and are especially liable to error for the most reactive compounds, with Y = Cl or CF_3; to reflect the relatively poor quality of the data only approximate times, $t_{1/2}$, for disappearance of half of the $TsiSiH(C_6H_4Y\text{-}p)I$ compounds are given (see Table 2), not rate constants. The possible errors are not such, however, as to cast doubt on the conclusion that the reaction is, as expected, and like the methanolysis, facilitated by electron-withdrawal by Y.

The results for the reactions of the iodides $TsiSiH(C_6H_4Y\text{-}p)I$ (0.02 *M*) with AgO_2CMe (the amount of which would have given an 0.05 *M* solution if it had all dissolved) must be treated with caution because they refer to a heterogeneous system, probably only about 10% of the silver salt being initially present in solution. Furthermore, the rates were again too high for accurate measurement by the techniques used, and in addition the iodide may have taken an appreciable time to dissolve. Puzzlingly, second order plots (based on the assumption that all the silver salt was in solution) were reasonably linear up to greater extent (up to > 70%) of reaction than were first order plots (linear up to ca. 50%), but we note that the kinetics of reactions of organic halides with silver salts are also very complex [17]. However, since all the reactions were carried out under similar conditions it is reasonable to compare the times for disappearance of a given amount of the initial iodide in each case; the times taken for the reaction to proceed from 20 to 60% disappearance of the iodide were used to give relative rates, k_{rel}, rather than those for the first 50% of reaction, because of the time taken for dissolution of the

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* Several people interested in the problem have written to us to suggest that the absence of rate acceleration by NaOMe in methanolysis of some $TsiSiMe_2X$ and TsiSiHRX species simply indicates that the attack of the nucleophile is not the rate-determining step, which is thus the loss of X^- from the five-coordinate intermediate. However, in such a process the rate would, in fact, be dependent on the concentration of the nucleophile, since the stationary concentration of the intermediate would be so dependent.

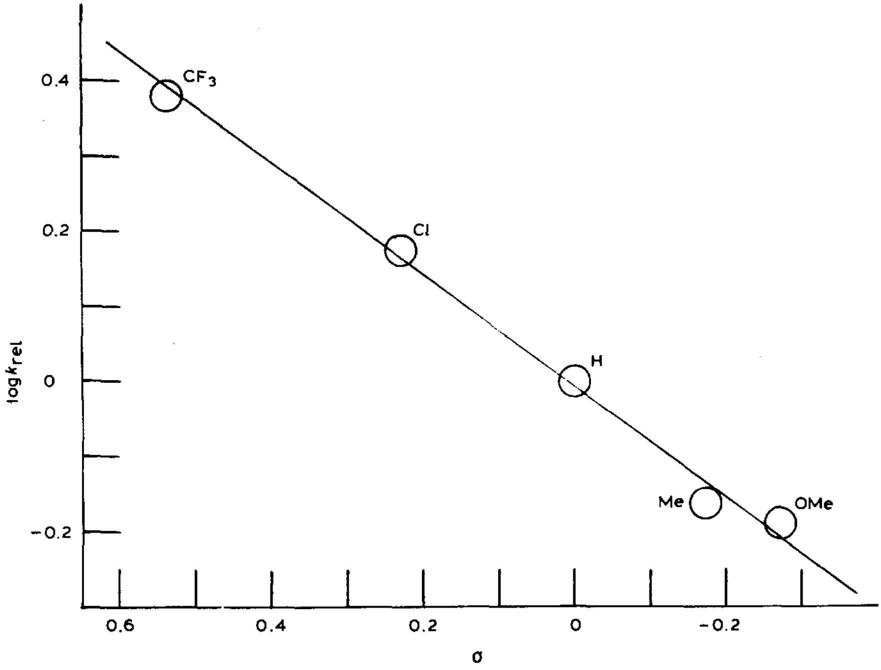

Fig. 1. Plot of log k_{rel} against σ for the solvolysis of TsiSiH(C_6H_4Y-*p*)I compounds in 1/1 v/v MeOH/dioxane at 35 °C.

reactants and the errors in timing immediately after mixing of the reactants in these rapid processes. In spite of the experimental uncertainty and the low overall spread of rates, the observed rates fall consistently with decrease in electron release by Y, as would be expected for rate-determining abstraction of I^-. The smallness of the substituent effects could be associated, as least in part, with the fact that formation of a bridged-species analogous to I will reduce the degree of positive charge on the functional silicon centre; calculations on model species suggest that the positive charge in a cation of type I would largely be divided between the α- and γ-Si centres [18]. However, it is possible that the rate of dissolution of the silver salt as some of it present in solution is used up may be in part limiting the rate, especially for the most reactive of the iodides. The feature of significance, however, is that the

Table 2

Reactions of TsiSiH(C_6H_4Y-*p*)I compounds (0.020 *M*) with KSCN (0.030 *M*) in MeCN at 35 °C

Y	$t_{1/2}$ (min) [a]	k_{rel}
MeO	7.8	0.76
Me	6.4	0.92
H	5.9	1.0
Cl	3.1	2.1
CF_3	0.9	6.5

[a] Time for consumption of half of the iodide.

substituent effects are in the opposite direction to those in the methanolysis and in the reaction with KSCN.

We can, it seems, rule out an S_N2(intermediate) mechanism for the alcoholysis of the iodides TsiSiH(C_6H_4Y-*p*)I, and thus by implication for those of the compounds $TsiSiMe_2X$ with X = I, $OClO_3$, or OSO_2CF_3, and can conclude that the alcohol must be involved in covalent bond formation in the transition state, not just nucleophilic solvation. We are then left with the question of why the methanolysis of TsiSiHPhX species is accelerated by NaOMe for X = Br, ONO_2, OSO_2Me etc., but not for X = I (or for reactions of $TsiSiMe_2X$ with X = I, $OClO_3$, or OSO_2CF_3), implying a duality of mechanism *. If it were only the iodides that showed unusual behaviour, this could possibly be associated with the joint influence of the bulk of the solvated methoxide ion and the bulk of the iodide ligand, but the triflate and perchlorate ligands should not provide any especially large steric hindrance, and hindrance should in any case be markedly smaller with TsiSiHRI compounds. The possibility that the acceleration by base might be associated with ligands of very high leaving group ability seems to be ruled out by the observation that in the reactions of TsiSiHPhX [10] and $TsiSiMe_2X$ [19] in MeOH alone the nitrates are actually more reactive than the iodides, and this is also the case in the reactions of the $TsiSiMe_2X$ compounds with KSCN in MeCN [19]. For the present we propose simply to designate the unusual methanolysis of TsiSiHPhI and $TsiSiMe_2X$ (X = I, $OClO_3$, OSO_2CF_3) as an S_N2(NBC) (bimolecular non-base-catalysed) process (indicative of the observed behaviour, not the mechanism), reflecting the conclusion reached in this paper that the methanol is covalently involved in the route to the rate-determining transition state.

The conclusion that the solvent is involved in nucleophilic attack on silicon in the methanolysis of $TsiSiMe_2X$ species provides a simple explanation of the fact that for X = $OClO_3$ [10] and OSO_2CF_3 [13] the solvolysis is markedly accelerated by the presence of water, with the acceleration proportional to the amount of water present, and the product diverted to the hydroxide, $TsiSiMe_2OH$. Evidently the smaller water molecule is taking the place of methanol as the nucleophile engaged in bond-formation to silicon. (This seemingly obvious explanation was rejected in our earlier discussion [10] because the absence of acceleration by base seemed to rule out rate-determining nucleophilic attack.) However, the acceleration by water is markedly smaller in the case of the iodides TsiSiHRI (R = Ph or Me) [10] and $TsiSiMe_2I$ [9]; for TsiSiHRI species this could be understood in terms of decreased steric hindrance at the silicon centre bearing a hydrogen atom (and so a lower sensitivity towards the bulk of the nucleophile), but the much lower sensitivity of $TsiSiMe_2I$ than of $TsiSiMe_2OClO_3$ or $TsiSiMe_2OSO_2CF_3$ towards the presence of water is difficult to explain.

We finally note that some features of the comparison [9] of the reactivities of t-Bu_3SiI and $TsiSiMe_2I$ in reactions previously tentatively assumed to be of the S_N2(intermediate) type now require rediscussion. For the moment we confine ourselves to the observation that the much greater sensitivity of t-Bu_3SiI than of

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* We should note here that other anions, e.g. N_3^-, F^-, and SCN^-, do carry out bimolecular attack on $TsiSiMe_2I$ even in MeOH. We assume that the effective bulk of these ions when solvated in MeOH is markedly smaller than that of the solvated MeO^- ion.

$TsiSiMe_2I$ towards the presence of water in methanol is consistent with our view that the former iodide is the more sterically hindered.

Experimental

Starting materials

The preparation of the $TsiSiH(C_6H_4Y\text{-}p)I$ compounds are described elsewhere [20,21].

Solvents were dried by standard methods.

Products

Products were isolated only for reactions of the parent species TsiSiHPhI. In this case they were shown to be the expected TsiSiHPhX compounds with X = OMe, NCS, or O_2CMe by comparison of their properties with those of authentic samples [11,20]. In other cases the identities of the products were confirmed by their mass spectra (all showing strong $[M - Me]^+$ peaks).

Rate measurements

For the methanolysis $TsiSiH(C_6H_4Y\text{-}p)I$ (ca. 0.04 mmol) was placed in an NMR tube and 1.0 cm^3 of a 1/1 v/v mixture of MeOH/dioxane, prewarmed to 35 °C, was added. The tube was capped, vigorously shaken, and placed in the probe of the spectrometer. The ^1H NMR spectrum was recorded at appropriate times and the heights, h and h', of the Tsi peak for the substrate and product, respectively, were noted. (The peak for the product was in all cases shifted by ca. 0.1 ppm upfield from that for the iodide.) Plots of $\ln(h/h + h')$ against time were good straight lines up to > ca. 80% completion of the reaction. The derived rate constants, k, and the half-lives, $t_{1/2}$, are shown in Table 1.

A similar procedure was used for the KSCN reactions, the iodide (0.020 mmol) being dissolved in 1.00 cm^3 of an 0.030 M solution of KSCN in MeCN. The appropriate second-order plots were good straight lines up to > 70% completion of the reaction. The plots were, however, used only for derivation of the time, $t_{1/2}$, taken for consumption of half of the iodide, and the values are listed in Table 2.

For reactions with AgO_2CMe, the iodide (0.020 mmol) and the AgO_2CMe (0.050 mmol) were placed in the NMR tube and glacial $MeCO_2H$ (1.00 cm^3) was added. The tube was capped and shaken, then placed in the probe of the spectrometer at

Table 3

Reactions of $TsiSiH(C_6H_4Y\text{-}p)I$ compounds (0.020 mmol) with AgO_2CMe (0.050 mmol) in $MeCO_2H$ (1.00 cm^3) at 35 °C [a]

Y	$t_{(20-60\%)}$ [b]	k_{rel}
MeO	5.5	1.5
Me	7.0	1.2
H	8.3	1.0
Cl	9.2	0.9
CF_3	11.5	0.7

[a] Only about one-tenth of the Ag_2OCMe would have dissolved initially. [b] Approximate time taken for reaction to go from 20 to 60% completion.

35 °C. From plots of $h/(h+h')$ against time, the times, $t_{(20-60\%)}$ between 20 and 60% consumption of the iodide were estimated, and are shown in Table 3. (Second order plots based on the assumption that all the silver salt was in solution (surprisingly) gave quite good straight lines up to > 75%, and first-order plots were linear up to ca. 50% completion of the reaction.)

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