An S_N2 (Intermediate) Mechanism for Solvolysis of Organosilicon Iodides?

Saman A. I. Al-Shali, Colin Eaborn,* Faraedon A. Fattah, and Sabah T. Najim

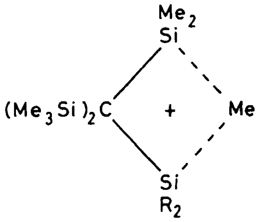
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K.

The hydrolysis (in H_2O–MeCN or H_2O–Me_2SO) and methanolysis of TsiSiR$_2$I [Tsi = $(Me_3Si)_3C$; R = Ph or Et] give only unrearranged products TsiSiR$_2$Y (Y = OH or OMe); thus the methanolyses of TsiSiMe$_2$I and TsiSiPhHI seem likely to be S_N2(intermediate) rather than S_N1 processes as previously suggested.

In recent years we have shown that some reactions of highly sterically hindered organosilicon iodides of the type TsiSiR$_2$I [Tsi = $(Me_3Si)_3C$] (*e.g.*, R = Ph or Et), *viz*. (a) reactions with silver or mercury(II) salts,[1] (b) photo-assisted[2] and oxidatively-assisted[3] solvolyses, (c) solvolysis in trifluoroacetic acid,[1] and (d) reactions with iodine monochloride,[4] probably involve silico-cationic intermediates. All these reactions are accompanied by 1,3-migration of a methyl group, to give products of the type $(Me_3Si)_2C(SiR_2Me)(SiMe_2Y)$, and are thought to involve bridged cations of the type (**1**) as intermediates.

In the light of the observation that the rates of methanolysis of the derivatives TsiSiMe$_2$X (X = $OClO_3$ or I) and TsiSiRHI (R = Me or Ph) are not significantly enhanced by the presence of NaOMe, we suggested that these also proceeded through silico-cations, formed in the rate-determining step in an S_N1 type of process;[5,6] in doing this we were applying the reasoning which led to the conclusion, accepted for many years, that the solvolysis of t-butyl halides is an S_N1 process.[7] Recently, however, evidence has been obtained that the solvolysis of t-butyl chloride, although involving rate-determining formation of an ion-pair (the cationic portion of which can then be attacked by nucleophiles or bases to give substitution or elimination products), is not a true S_N1 process, since solvent is nucleophilically involved in the transition state (which does, however, have considerable ionic character); this mechanism has been termed S_N2(intermediate).[8] It was thus of importance to determine whether the solvolyses of TsiSiR$_2$X species which are not catalysed by base are, in fact, true S_N1 processes, with no nucleophilic involvement of solvent in the rate-determining step, in which case formation of the bridged ions (**1**), and hence of rearranged products, would be expected.

We looked initially at the hydrolysis of TsiSiPh$_2$I and TsiSiEt$_2$I, the former in (i) H_2O–MeCN (5 vol-%) for 60 days under reflux and (ii) H_2O–Me_2SO (20 vol-%) for 24 h under reflux, and the latter in H_2O–MeCN (0.5 and 2 vol-%) for 25 days at 60 °C. In every case the product was exclusively the unrearranged hydroxide, TsiSiR$_2$OH [^{1}H n.m.r. (CCl$_4$), R = Ph, δ 0.22 (s, 27H, SiMe$_3$), 2.02 (s, 1H, OH), and 7.2—8.0 (s, 10H, Ph); R = Et, δ 0.21 (s, 27H, SiMe$_3$), 1.25 (s, 1H, OH), and 0.8—1.1 (m, 10H, Et)].† We then looked at the rather slower methanolysis of TsiSiEt$_2$I. (With TsiSiPh$_2$I the reaction is too slow for study.) After 42 days under reflux the product was exclusively TsiSiEt$_2$OMe. [In contrast, the reaction of the iodide for 5 min with refluxing MeOH containing AgClO$_4$ gave TsiSiEt$_2$OMe and $(Me_3Si)_2C(SiEt_2Me)(SiMe_2OMe)$ in *ca*. 1:1 ratio.] We conclude that the hydrolysis of TsiSiPh$_2$I and TsiSiEt$_2$I, and the methanolysis of TsiSiEt$_2$I (and by implication that of TsiSiMe$_2$I and TsiSiPhHI) do not involve nucleophile-free silico-cationic intermediates, and certainly not the bridged species (**1**).



(**1**)

There is thus now evidence for the existence of three distinct mechanisms for the solvolysis of TsiSiRR′X species, *viz* in (a) the solvolysis of TsiSiEt$_2$I in CF_3CO_2H, which proceeds with rearrangement and which is not catalysed by NaO_2CCF_3, and so appears to be an S_N1 process;[1] (b) the methanolyses of TsiSiPhHX species (X = Br, F, ONO_2, NCO, NCS, and $OSO_2C_6H_4Me$-*p*), which are powerfully catalysed by NaOMe, and so appear to be S_N2 processes;[5,9] and (c) the methanolyses

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† The compound TsiSiEt$_2$OH can be made very readily by treatment of TsiSiEt$_2$H with KMnO$_4$ in MeOH.

of $TsiSiMe_2OClO_3$, $TsiSiMe_2I$, and TsiSiPhHI which are not catalysed by NaOMe, but which do not, as judged by the absence of rearrangement in the case of $TsiSiEt_2I$, involve a silico-cationic intermediate. It is reasonable to assume that the mechanistic spectrum is similar to that for alkyl halides,[8] and thus that the last mentioned type of process has an S_N2(intermediate) mechanism. It is conceivable that the perchlorate $TsiSiMe_2OClO_3$, with its much better leaving group, could react by an S_N1 mechanism (we have not yet been able to make a perchlorate which would enable us to detect rearrangement), but the operation of an S_N2(intermediate) mechanism would account for the fact (which we previously found difficult to reconcile with an S_N1 mechanism) that the perchlorate reacts only very slowly, if at all, with CF_3CH_2OH,[5] in which S_N1 processes would be expected to occur more readily than in MeOH.[8]

It is noteworthy that Dewar and Healey have recently argued that the differences in behaviour between carbon and silicon compounds in nucleophilic substitution are predominantly attributable to the smaller size of the carbon atom, which results in marked steric hindrance to formation of penta-co-ordinate species, and not, for example, to the use of d-orbitals by silicon;[10] the growing body of evidence that highly sterically hindered organosilicon iodides show very close mechanistic similarity to alkyl iodides is nicely consistent with their view.

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