Oxidatively Assisted Nucleophilic Substitution of Organosilicon Iodides

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The iodides $(Me_3Si)_3CSiMe_2I$, $(Me_3Si)_3CSiPh_2I$, and Bu^t_3SiI react with *m*-chloroperoxybenzoic acid to give the hydroxides $(Me_3Si)_3CSiMe_2OH$, $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$, and Bu^t_3SiOH, respectively, in MeOH alone, and the corresponding chlorides in the presence of LiCl; the formation of rearranged products from $(Me_3Si)_3CSiPh_2I$ suggests the participation of silico-cationic intermediates.

The chemistry of organosilicon halides is normally dominated by the ease of direct bimolecular nucleophilic displacements, which prevents observation of other possible mechanisms. When very large steric hindrance is introduced into the organosilicon species the direct substitution is inhibited, and it is sometimes possible to detect other reactions;[1] examples of this are provided by the reactions of tris(trimethylsilyl)methylsilicon compounds of the type $TsiSiR_2I$ [Tsi = 'trisyl' = $(Me_3Si)_3C$] with (a) electrophilic reagents,[2,3] and (b) methanol under u.v. irradiation.[4] Both of these reactions appear to involve silico-cationic intermediates, and, especially for (b), show a close similarity to the reactions of some alkyl iodides under similar conditions. We now report on the reactions of some sterically hindered organosilicon iodides (**1**)—(**3**) with *m*-chloroperoxybenzoic acid (*m*-CPBA) (under conditions in which ordinary organosilicon iodides would undergo rapid methanolysis or hydrolysis), and show that there is again a previously hidden close similarity to the behaviour of alkyl iodides,[5–7] though there are some understandable differences.

$TsiSiMe_2I$ (**1**)
$TsiSiPh_2I$ (**2**)
Bu^t_3SiI (**3**)
$TsiSiMe_2OH$ (**4**)
$(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$ (**5**)
Bu^t_3SiOH (**6**)

$Tsi = (Me_3Si)_3C$

Compound (**1**) reacts readily with *m*-CPBA in MeOH at room temperature (*ca.* 21 °C) to give exclusively the silanol (**4**). Monitoring by ^1H n.m.r. spectroscopy of reactions in MeOH

(15 cm^3) of (**1**) (0.40 g, 1.0 mmol) with (a) 0.65 g (*ca.* 3.3 mmol), (b) 1.30 g (*ca.* 6.5 mmol), and (c) 2.60 g (*ca.* 13 mmol) of *m*-CPBA showed that after 10 min *ca.* (a) 35, (b) 52, and (c) 65% of (**1**) had reacted, and *ca.* (a) 30, (b) 7, and (c) 2.5 h were required for complete reaction.† The presence of LiCl increased the rate of disappearance of (**1**) and diverted the reaction wholly to formation of the chloride $TsiSiMe_2Cl$; thus for reactions in MeOH (8 cm^3) at 30 °C between (**1**) (0.25 mmol) and *m*-CPBA (1.7 mmol) (a) alone or (b) in the presence of LiCl (2.4 mmol), 50% of the (**1**) disappeared in *ca.* (a) 37 and (b) 10 min, and 90% in *ca.* (a) 150 and (b) 20 min. No reaction took place at room temperature between (**1**) (0.84 mmol) and *m*-CPBA (*ca.* 6.0 mmol) in MeOH (20 cm^3) containing $LiNO_3$ (10 mmol). The reaction between (**1**) and *m*-CPBA was slower in Bu^tOH than in MeOH, and the product was again (**4**). Reaction of (**1**) (0.48 mmol) with *m*-CPBA (*ca.* 5 mmol) in n-pentane (20 cm^3) at room temperature was 50% complete in *ca.* 1 h, and 90% complete in *ca.* 6 h, the product again being exclusively (**4**).

When the diphenyl iodide (**2**) was used, the product from the reaction with *m*-CPBA in MeOH was exclusively the *rearranged* silanol (**5**). Reaction between (**2**) (0.4 mmol) and *m*-CPBA (6 mmol) in MeOH (15 cm^3) at room temperature was 50% complete in 2 h and 90% in 10 h. In a reaction between (**2**) (0.18 mmol) and *m*-CPBA (1.65 mmol) in MeOH (8 cm^3) in the presence of LiCl (2.4 mmol), 30% of (**2**) disappeared in *ca.* 50 min but the rate then fell off and the reaction became very slow after reaching *ca.* 50% completion in 6 h; addition of more LiCl (2.4 mmol) then restored the rate, so that after an additional 8 h the reaction was *ca.* 90% complete. The product was exclusively the rearranged chloride $(Me_3Si)_2C(SiPh_2Me)(SiMe_2Cl)$.

To confirm that the reactions were not confined to trisylsilicon derivatives, the behaviour of (**3**)[8] was examined. This compound reacted with *m*-CPBA in MeOH markedly more slowly than (**1**), but the results were more quantitatively reproducible and some rough kinetic studies were possible. With (**3**) (0.34 mmol) and *m*-CPBA (5 mmol) in MeOH (15 cm^3) at room temperature, reaction to give exclusively (**6**) was half complete in *ca.* 3.5 h, and a good first order plot was obtained for the disappearance of (**3**) up to 86% of reaction, after which there was a marked fall in rate. With 0.34 mmol of (**3**) and 2.5 mmol of *m*-CPBA, the half-life was *ca.* 7 h and a first order plot was obtained up to 70% reaction, whereas with 0.35 mmol of (**3**) and 1.25 mmol of *m*-CPBA, a first order plot was good only to 30% reaction (50% took *ca.* 30 h). The slopes of the first order plots for the first two runs above were approximately proportional to the initial concentration of the *m*-CPBA, indicating that in the early stages at least, the reaction is apparently first order with respect to the acid when a large excess of the latter is present. It seems, however, that even when there is a considerable excess of the acid much of it is consumed during the reaction (*cf.* ref. 7). (Reactions with alkyl iodides in the presence of lithium chloride are known to produce lithium iodate,[5] so that at least 3 mol of the acid could be destroyed for each mol of iodide consumed.) Thus in the reaction mentioned above involving 0.35 mmol of (**3**) and 1.25 mmol of *m*-CPBA the reaction ceased after 45 h when 55% of (**3**) had reacted, but addition after 90 h of an additional 1.25 mmol of the acid restarted the reaction, which then reached 92% completion after a further 90 h. (For preparative purposes, unless a large excess of the acid is used, it seems better to add it in portions at appropriate stages in order to ensure fairly rapid completion of the reaction.) Rather surprisingly the presence of LiCl (2.5 mmol) greatly reduced the rate of reaction between (**3**) (0.48 mmol) and *m*-CPBA (1.7 mmol) in MeOH (15 cm^3), only 10% of (**3**) being consumed (to give Bu^t_3SiCl) in 24 h. The presence of $LiNO_3$, while markedly reducing the rate of reaction of (**3**) did not completely inhibit it; the product was the silanol.

The points of similarity to the reactions of alkyl iodides[5–7] are: (i) the need to use a substantial excess of *m*-CPBA to ensure reasonably rapid and complete reaction; (ii) the occurrence in the case of (**2**) of rearrangements which can be interpreted in terms of cationic intermediates; and (iii) the acceleration of the reaction [in the case of (**1**) and (**2**)] by LiCl and the diversion of the reactions to formation of chlorides. Differences between the reactions of the organosilicon and those of the alkyl iodides are: (i) exclusive formation of hydroxide products from the silicon iodides in MeOH, compared with predominant formation of methyl ethers from alkyl iodides; this can be attributed to greater steric hindrance to attachment of the MeO than of the HO group (derived from the water in the *m*-CPBA) at the crowded silicon centres; (ii) the (expected) absence of olefin analogues in the products from the silicon compounds.

The reactions of the alkyl iodides have been discussed in terms of oxidation of the iodide ligand to a better leaving group, such as IO_n (or after rearrangement, OIO_{n-1}), which is then either displaced by attack of a nucleophile or leaves to give a carbocation, which is then trapped by a nucleophile,[5–7] and similar processes can be assumed for reaction of the organosilicon iodides. The production of chlorides from (**1**) and (**2**), and especially of the rearranged product in the latter case, can be nicely interpreted in terms of formation of a silicocation (probably a methyl-bridged species[1,2]), but this would not account for the acceleration of the reaction by LiCl. Since the reactions in the presence of an excess of LiCl can greatly slow down or stop after partial disappearance of the organosilicon iodides and [at least in the case of (**2**)] the rate can then be restored by addition of more LiCl, it seems that Cl^- and (thus presumably) *m*-CPBA are consumed in some competing process (possibly involving oxidation to ClO_n species), and the much lower rate of reaction in the case of (**3**) may allow this process to dominate.

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† Following precedent,[5] the *m*-CPBA used (Aldrich 80—90%), which contains water, is for convenience assumed to have an effective molecular weight of 200 rather than the value of 173 appropriate to the anhydrous material.