Photo-induced Reactions of an Organosilicon Iodide

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Summary The results of u.v. irradiation of $(Me_3Si)_3CSiPh_2I$ in MeOH, n-C_6H_{14}, CCl_4, Et_2O, and PhOMe are interpreted in terms of the formation of cationic as well as free-radical organosilicon intermediates.

The 'trisyl' compounds $TsiSiPh_2F$ and $TsiSiPh_2I$ [where 'trisyl' refers to the $(Me_3Si)_3C$ group, symbolized by Tsi] undergo unusual reactions on pyrolysis, the former by a molecular elimination and the latter apparently by a free-radical process.[1,2] It was thus of interest to see whether u.v. irradiation would initiate reactions of these compounds, and we find that while the fluoride is unaffected by irradiation in MeOH (as is the corresponding bromide), novel reactions of the iodide are initiated in this and other media. Some of the products of the photolytic reactions seem, however, to come from ionic rather than free radical intermediates.

Brief details of results of irradiations are given in the Table; the product compositions listed are rough values derived from the ratio of the integrated ^1H n.m.r. signal from the Me_3Si or Me_2Si groups of the compound concerned to that from all the phenyl groups in the mixture.† The main features are as follows. (a) Irradiation induces methanolysis of the iodide (no significant reaction occurs in the absence of irradiation), to give a roughly 2 : 1 mixture of rearranged and unrearranged methoxides, $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OMe)$ (**2b**) and $TsiSiPh_2OMe$ (**2a**). The presence of 0·1 M NaOMe, 1% H_2O, or O_2 does not significantly affect the product composition, except that in the presence of NaOMe an additional, unidentified, product is formed at the expense of starting material. (b) In the presence of $LiNO_3$ some rearranged nitrate $(Me_3Si)_2C(SiPh_2Me)(SiMe_2ONO_2)$ (**3**) is formed. (c) Irradiation in hexane for 2 h gives the rearranged iodide $(Me_3Si)_2C(SiPh_2Me)(SiMe_2I)$ (**1b**), and other (unidentified) products. With oxygen bubbling through the reaction medium, no starting material or rearranged iodide is present after 2 h, and a complex mixture of other products (unidentified) is formed. (d) Irradiation in Et_2O gives rearranged iodide and unidentified products, which do not include any significant amounts of SiOEt species. Irradiation in PhOMe for 1 h gives rearranged iodide and unidentified products, but after 9 h very little original or rearranged iodide remains, and the major product is the cyclized species (**5**), which is also formed in the pyrolysis of $TsiSiPh_2I$.[2] (e) Irradiation in CCl_4 gives a mixture of products, including the unrearranged chloride $TsiSiPh_2Cl$ (**4**) but not the rearranged chloride $(Me_3Si)_2C(SiPh_2Me)(SiMe_2Cl)$.

$TsiSiPh_2I$ (**1a**)
$(Me_3Si)_2C(SiPh_2Me)(SiMe_2I)$ (**1b**)
$TsiSiPh_2OMe$ (**2a**)
$(Me_3Si)_2C(SiPh_2Me)(SiMe_2OMe)$ (**2b**)
$(Me_3Si)_2C(SiPh_2Me)(SiMe_2ONO_2)$ (**3**)
$TsiSiPh_2Cl$ (**4**)

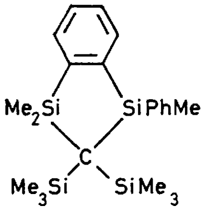
Table. Products from irradiation of $(Me_3Si)_3CSiPh_2I$.[a]

Medium	Time/h	Products (yield/%)
MeOH	1	(**1a**), (37); (**2a**), (17); (**2b**), (40)
MeOH, NaOMe (0·1 M)	1	(**1a**), (7); (**2a**), (19); (**2b**), (53)
MeOH: H_2O (99 : 1 *v/v*)	1	(**1a**), (31); (**2a**), (17); (**2b**), (42)
MeOH + $LiNO_3$ (3 M)	3	(**1a**), (27); (**2a**), (15); (**2b**), (43); (**3**), (12)
MeOH, O_2	1	(**1**), (28); (**2a**), (19); (**2b**), (35)
CCl_4	2	(**1a**), (55); (**4**), (11); I_2
n-C_6H_{14}	2	(**1a**), (30); (**1b**), (48)
n-C_6H_{14}, O_2[b]	2	No (**1a**) or (**1b**); u.m.
PhOMe	1	(**1a**), (27); (**1b**), (47)
	9	(**1b**), (4); (**5**), major product
Et_2O	3	(**1a**), (19); (**1b**), (31); no SiOEt products

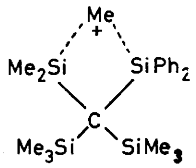
u.m. = unidentified material.

[a] The quartz reaction vessel was irradiated from a distance of 10 cm with a Hanovia medium pressure Hg lamp, Model U.V.S. 500. Products were normally identified *in situ* from their ^1H n.m.r. spectra, but for the reactions in CCl_4 and PhOMe they were first separated by g.l.c. [b] Oxygen was bubbled through the solution during irradiation.

† The extent of reaction sometimes varied from run to run under seemingly identical conditions, so the discussion concentrates mainly on product ratios.



(5)



(6)

The formation of methoxide products from methanol is most unlikely to involve attack of silicon-centred radicals on the solvent; there is no known example of such an S_H2 displacement at oxygen by a silicon radical, and $Me_3Si\cdot$ radicals do not react by this mechanism with MeOH.[3] The formation of rearranged nitrate in the presence of $LiNO_3$ parallels that observed in methanolysis of $TsiSiPh_2I$ assisted by silver and mercury(II) salts,[4] and points strongly to a cationic intermediate, presumably the bridged cation (**6**).[4] On the other hand, the influence of oxygen on the reaction in hexane suggests that free-radical species are also produced by irradiation. In fact, the results show a remarkable similarity to those observed by Kropp and colleagues for irradiation of alkyl iodides in similar media,‡ and can be interpreted in terms of a sequence, shown in Scheme 1, analogous to that which they proposed.[5] In this sequence, irradiation gives a radical pair [Si• I•], which can be trapped or revert to an iodide, or can, by electron transfer, give an ion pair $[Si^+ \; I^-]$. As with the alkyl iodides,[5] the cations produced may be more energetic than those formed in ordinary solvolyses, and this would account for the fact that unrearranged methoxide is formed in the photolysis but not in methanolysis promoted by silver or mercury(II) salts.[4]§

$$\begin{tikzcd}
\geqslant SiI \arrow[r, shift left, "h\nu"] & {[\geqslant Si\cdot \; I\cdot]} \arrow[l, shift left] \arrow[r] \arrow[d] & {[\geqslant Si^+ \; I^-]} \arrow[d] \\
 & \text{products} & \text{products}
\end{tikzcd}$$

Scheme 1.

However, we cannot rule out the independent formation of radical and ionic species as in Scheme 2.

$$\begin{tikzcd}
{[\geqslant Si\cdot \; I\cdot]} \arrow[d] & \geqslant SiI \arrow[l, "h\nu"'] \arrow[r, "h\nu"] & {[\geqslant Si^+ \; I^-]} \arrow[d] \\
\text{products} & & \text{products}
\end{tikzcd}$$

Scheme 2.

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‡ The main differences are those expected: *viz.* the absence in the organosilicon reactions of elimination products and of products of hydrogen-atom abstraction by silicon-centred radicals.

§ In contrast to Kropp *et al.*,[5] we think that the ion pair must be substantially solvated.

[1] C. Eaborn, D. A. R. Happer, P. B. Hitchcock, S. P. Hopper, K. D. Safa, S. S. Washburne, and D. R. M. Walton, *J. Organomet. Chem.*, 1980, **186**, 309.
[2] C. Eaborn and K. D. Safa, *J. Organomet. Chem.*, 1980, **204**, 169.
[3] B. J. Cornett, K. Y. Choo, and P. P. Gaspar, *J. Am. Chem. Soc.*, 1980, **102**, 377.
[4] C. Eaborn, D. A. R. Happer, S. P. Hopper, and K. D. Safa, *J. Organomet. Chem.*, 1979, **170**, C9; 1980, **188**, 179.
[5] P. J. Kropp, T. H. Jones, and G. S. Poindexter, *J. Am. Chem. Soc.*, 1973, **95**, 5420; G. S. Poindexter and P. J. Kropp, *ibid.*, 1976, **98**, 4319; P. J. Kropp, G. S. Poindexter, N. J. Pienta, and D. C. Hamilton, *ibid.*, p. 8135.