Photoinduced Ionic and Free-radical Reactions of Some Organosilicon Iodides

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U.v. irradiation (medium-pressure Hg lamp) induces reaction of $TsiSiPh_2I$ (1a) [Tsi = $(Me_3Si)_3C$] with methanol to give both the unrearranged and rearranged methoxides $TsiSiPh_2OMe$ and $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OMe)$; in the presence of $LiNO_3$ some $(Me_3Si)_2C(SiPh_2Me)(SiMe_2ONO_2)$ is also formed. The analogous solvolysis in $PhNH_2$ gives the rearranged anilide $(Me_3Si)_2C(SiPh_2Me)(SiMe_2NHPh)$. These reactions are thought to involve the intermediate formation of a silico-cation. On the other hand the exclusive formation of the unrearranged chloride $TsiSiPh_2Cl$ upon irradiation in CCl_4 appears to involve a free-radical process. The photoinduced rearrangement of (1a) to $(Me_3Si)_2C(SiPh_2Me)(SiMe_2I)$ in $n-C_5H_{12}$, $n-C_6H_{14}$, Et_2O, and PhOMe may involve a cationic intermediate, but a free radical rearrangement cannot be ruled out; the subsequent formation of a disilaindane derivative (6) in PhOMe probably involves cyclization of a free radical. The iodide TsiSiPhMeI also undergoes rearrangement to $(Me_3Si)_2C(SiPhMe_2)(SiMe_2I)$ upon irradiation in $n-C_5H_{12}$. The methanolysis of $TsiSiMe_2I$ is also photo-catalysed, though less effectively than that of (1a).

Trisyl silicon compounds of the type $TsiSiR_2X$ [where trisyl denotes tris(trimethylsilyl)methyl, symbolized by Tsi] are known to display highly unusual behaviour as a consequence of the severe steric strain in the molecule.[1-7] One aspect of this is the ready pyrolysis of the compounds $TsiSiPh_2F$ and $TsiSiPh_2I$, the former losing Me_3SiF by a molecular elimination and the latter losing HI by a free-radical process.[2,5] It was thus of interest to see whether these and related compounds would undergo photolysis.†

Results and Discussion

A preliminary survey of the reactions of $TsiSiPh_2X$ (X = F or I) with EtOH under u.v. irradiation, involving analysis of the products by linked g.l.c.–mass spectrometry, revealed that extensive reaction of the iodide $TsiSiPh_2I$ occurred, and no significant reaction of $TsiSiPh_2F$. For more detailed studies of this type of reaction of the iodide, methanol was used as the medium, since methanolysis of the iodide promoted by silver or mercury(II) salts has been extensively studied.[3] Subsequently, other solvents were also used for the photolysis studies, as described below.

The compositions of the mixtures produced by irradiation of $TsiSiPh_2I$ in various media with light from a medium-pressure mercury lamp, under nitrogen unless otherwise indicated, are shown in the Table. The compositions were determined by ^1H n.m.r. spectroscopy, with the help of g.l.c. where necessary, and are subject to substantial error, though not such as to affect the discussion below. [For example, we estimate that an apparent 20 : 40 ratio of (2a) to (2b) could be as low as 16 : 44 or as high as 24 : 36.] The emphasis in the discussion of the results is necessarily on the approximate product ratios rather than the extent of reaction, since the latter sometimes varied substantially between seemingly identical runs.

$TsiSiPh_2I$ (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)

$(Me_3Si)_2C(SiPh_2Me)(SiMe_2NHPh)$ (5)

It is clear that u.v. irradiation greatly facilitates the reaction of (1a) with methanol. [The irradiation raises the temperature of the solution, but no appreciable reaction occurs when a solution of (1a) in MeOH is refluxed for 4 days without irradiation.] Some features of the methanolysis results are that (a) the unrearranged and rearranged methoxides (2a) and (2b) were formed in a *ca.* 1 : 2.5 ratio in reaction in MeOH alone, and this ratio was not significantly affected by the presence of 0.1M-NaOMe, 0.6M-C_5H_5N, 1% H_2O, 1M-LiCl, 3M-$LiNO_3$, or O_2 (though small amounts of extra products were formed in this last case); (b) an unidentified product which was present in all cases was formed in larger amounts in the reaction in the presence of NaOMe, and it is possible that this accounts for the seemingly smaller amount of unchanged (1a); and (c) in the presence of $LiNO_3$ some rearranged nitrate (3) was formed, but no chloride became incorporated in the presence of LiCl.

The features of the remaining results are as follows. (a) Irradiation in aniline gave the rearranged solvolysis product (5). (b) Irradiation in hexane for 2 h gave the rearranged iodide (1b) and some unidentified products, along with 30% of the starting (1a); with oxygen bubbling through the solution no starting material or rearranged iodide was present after 2 h, a complex mixture of other (unidentified) products being formed. (c) Irradiation in Et_2O gave the rearranged iodide and unidentified products, which did not include any significant amounts of SiOEt species. Irradiation in PhOMe for 1 h gave rearranged iodide and a mixture of other (unidentified) products, but after 9 h very little original or rearranged iodide remained, and the major product was the cyclized species (6), which is also formed in the pyrolysis

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† A preliminary account has appeared.[8]

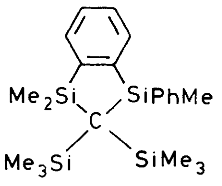
Products from irradiation of $(Me_3Si)_3CSiPh_2I$

Medium	Time (h)	Product composition (%) [a]
MeOH	1	(1a), 37; (2a), 17; (2b), 40
MeOH + NaOMe (0.1M)	1	(1a), 10; (2a), 20; (2b), 53
MeOH; H_2O (99 : 1 v/v)	1	(1a), 31; (2a), 17; (2b), 42 [b]
MeOH + $LiNO_3$ (3M)	3	(1a), 27; (2a), 15; (2b), 43; (3), 12
MeOH, LiCl (1M)	1	(1a), 14; (2a), 18; (2b), 50
MeOH, C_5H_5N (0.6M)	0.5	(1a), 80; (2a), <5; (2b), 15
	4	(1a), 12; (2a), 20; (2b), 50
MeOH, O_2 [c]	1	(1a), 28; (2a), 19; (2b), 35
$PhNH_2$	8	(5), >80
CCl_4	2	(1a), 55; (4), 11 [d]
n-C_5H_{12}	2	(1a), 26; (1b), 37
n-C_6H_{14}	2	(1a), 30; (1b), 48
n-C_6H_{14}, O_2 [c]	2	No (1a) or (1b)
PhOMe	1	(1a), 27; (1b), 47
	9	(1b), 4; (6)
	29	(6), major product
Et_2O	3	(1a), 19; (1b), 31 [e]

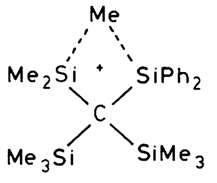
[a] Unidentified products account for the differences between the combined percentages and 100%. [b] No silanol products could be detected. [c] Oxygen was bubbled through the solution. [d] No rearranged chloride was present; I_2 was formed. [e] No SiOEt products were formed.

of $TsiSiPh_2I$.[5] (d) Irradiation in CCl_4 gave a mixture of products, including iodine and the unrearranged chloride $TsiSiPh_2Cl$ (4), but not the rearranged chloride $(Me_3Si)_2C(SiPh_2Me)(SiMe_2Cl)$. [Unrearranged chloride (4) but no rearranged chloride is formed when $TsiSiPh_2H$ reacts with CCl_4 under catalysis by $(PhCOO)_2$.[9]] The small extent of reaction in this case is probably real, and may possibly be associated with the presence of molecular iodine generated by the photolysis.

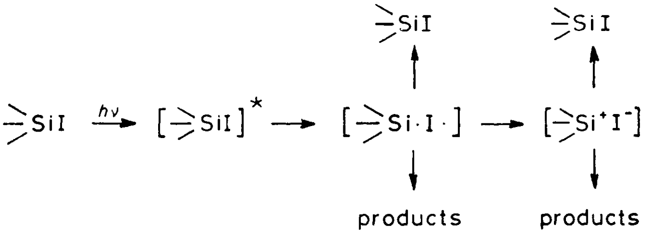
The formation of methoxide products from methanol is most unlikely to involve attack of silicon-centred radicals on the solvent; there is no known example of such an S_H2 displacement of hydrogen from oxygen by a silicon radical,* and $Me_3Si^{\cdot}$ radicals do not react by this mechanism with MeOH.[10] On the other hand, the formation of rearranged methoxide would be expected if the iodide (1a) underwent ionization upon irradiation, since rearranged products are exclusively formed when (1a) is treated with silver or mercury(II) salts in methanol, in reactions which are believed to proceed through the bridged cation (7).[3] The formation of the rearranged nitrate (3) in the presence of $LiNO_3$ points clearly to the intermediacy of a cation, nitrate (3) also being formed when (1a) is treated with $AgNO_3$ in methanol.[3] [The formation of some unrearranged methoxide (2a) in the photocatalysed methanolysis contrasts with the exclusive formation of (2b) in the solvolysis promoted by silver or mercury(II) salts, and this point is considered later.] The absence of any chloride product from the reaction in the presence of LiCl is consistent with the failure of chloride ion to trap the silico-cations formed from $TsiSiMe_2OClO_3$ in solvolysis.[6] The absence of hydroxide product(s) from the reaction in the presence of 1% of water is consistent with the results in reactions catalysed by silver salts, but contrasts with those in the solvolysis of the perchlorate $TsiSiMe_2OClO_3$.[6]



(6)



(7)



Scheme 1.

On the other hand the exclusive formation of the unrearranged chloride (4) upon irradiation of (1a) in CCl_4, and the marked influence of oxygen on the reaction in hexane, shows that free-radical species are also produced by the irradiation. In fact the results show a remarkable similarity to those observed by Kropp and his colleagues for irradiation of alkyl iodides in similar media,[11,12] and can be interpreted in terms of a sequence, shown in Scheme 1, analogous to that which they proposed. In this sequence, irradiation gives a radical pair [Si·I·] (*via* a photoexcited $\equiv$SiI species), which can sometimes be trapped (as for example in the reaction in CCl_4, or in hexane in the presence of oxygen) or can, by electron transfer, give an ion-pair [Si^+ I^-]. As with the alkyl iodides,[12] the cations produced may be more energetic, and thus less selective, than those formed in ordinary solvolysis, and this would account for the fact that some unrearranged methoxide (2a) is formed in the light-catalysed methanolysis but not in the methanolysis promoted by silver or mercury(II) salts; indeed, it is conceivable that, with an excess of energy available, some of the unbridged ion $TsiSiPh_2^+$ is present, and is trapped by the solvent. The main differences between the light-catalysed reactions of $TsiSiPh_2I$ and those of the alkyl iodides are those expected, *viz.* the absence in the organosilicon reactions of elimination products and of products formed by abstraction of hydrogen atoms by silicon-centred radicals. There are other minor differences; for example, whereas the carbocations produced by photolysis react with Et_2O to give $\geq$COEt products, the silico-cations seem not to cleave either Et_2O or PhOMe; for shorter exposure, the products formed in these solvents are somewhat similar to those in hexane. Another difference is that (as implied by the absence of rearranged products) the formation of $TsiSiPh_2Cl$ from reaction in CCl_4 is apparently a free-radical process, silicon-centred radicals being especially effective at abstracting halogens from carbon–halogen bonds,[13] whereas formation of alkyl chlorides from alkyl iodides in CH_2Cl_2 is believed to proceed through the cations.[11,12]

The formation of the rearranged iodide (1b) may proceed through cation (7) in hexane and ethers, but it is also possible that a small proportion of initially formed $TsiSiPh_2^{\cdot}$ radicals (free or within the radical pair) undergo rearrangement to $(Me_3Si)_2C(SiPh_2Me)(SiMe_2^{\cdot})$ radicals, so that in the absence of an efficient trap (such as CCl_4) for the initially formed radicals some products of such rearrangements are observed; such a rearrangement was postulated to account for the products from the pyrolysis of $TsiSiPh_2I$.[5] The cyclized product (6), formed on longer irradiation in PhOMe, can be most

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* An example of an S_H2 displacement of an alkyl group from oxygen by a $Cl_3Si^{\cdot}$ radical has recently been reported (R. A. Jackson, F. Malek, and N. Ozaslan, *J. Chem. Soc., Chem. Commun.*, 1981, 956).

simply interpreted in terms of photodissociation of the rearranged iodide (1b) to give the radical $(Me_3Si)_2C(SiPh_2Me)(SiMe_2^{\cdot})$, since the latter was the postulated intermediate in the formation of (6) in the pyrolysis of $TsiSiPh_2I$ [a rearrangement of the radical $TsiSiPh_2^{\cdot}$ to $(Me_3Si)_2C(SiPh_2Me)(SiMe_2^{\cdot})$ under those conditions being assumed].[5] The absence of aromatic substitution products, such as $TsiSiPh_2(C_6H_4OMe)$ from the reaction in anisole is noteworthy, since it contrasts with the formation of alkylated aromatic compounds in the photocatalysed reactions of alkyl iodides in aromatic solvents.[12] It is possible that any $Si-C_6H_4OMe$ bonds formed would be cleaved by the hydrogen iodide produced at the same time, but we note that the Si–Ph bond of (6) survives in the reaction in anisole, although HI must again be formed. It is more likely that attack of the radical $TsiSiPh_2^{\cdot}$ on anisole is sterically inhibited, while the rearranged radical $(Me_3Si)_2C(SiPh_2Me)(SiMe_2^{\cdot})$ more readily undergoes cyclization to give (6).[5] Since $Me_3Si^{\cdot}$ radicals can attack aromatic solvents,[13,14] further investigation of photocatalysed reactions of $TsiSiR_2I$ species in such solvents would be of interest.

The related iodide TsiSiPhMeI was found to undergo rearrangement to $(Me_3Si)_2C(SiPhMe_2)(SiMe_2I)$ upon irradiation in pentane; after 1 h the original and rearranged iodides constituted approximately 67 and 21%, respectively, of the mixture, after 2 h 43 and 32%, and after 4 h <10 and 45%. Other species are evidently formed, possibly including the analogue of the cyclic compound (6). The reaction of the dimethyl compound $TsiSiMe_2I$ with MeOH was also catalysed by irradiation, though much less effectively than that of (1a). After 1 h, the starting material comprised 75% and the solvolysis product $TsiSiMe_2OMe$ 25% of the mixture, and the corresponding percentages at various later times were: 4 h, 45 and 55%; 8 h, 35 and 65%; 14 h, 20 and 80%; 20 h, 15 and 85% (approximating to a first-order process); there were no other products. By comparison, <10% of the methoxide is formed upon refluxing the $TsiSiMe_2I$ in methanol for 24 h. The much more effective catalysis with $TsiSiPh_2I$ than with $TsiSiMe_2I$ might possibly originate in the absorption of radiation by the Ph groups of the former, only the weaker absorption by the Si–I bond being available for the latter. (Brief details of the u.v. spectra are given in the Experimental section.) Alternatively, there might be more return to the starting iodide within the radical pair in the case of the less hindered dimethyl compound. In an attempt to induce photosensitization (*cf.* ref. 12), a solution of $TsiSiMe_2I$ in a 3 : 7 v/v benzene–methanol mixture was irradiated for 8 h, but the ratio of unchanged iodide to methoxide after this time, *viz.* 38 : 62, was virtually identical to that observed for reaction in methanol alone.

No reaction took place when the bromide $TsiSiPh_2Br$ was irradiated in MeOH for 5 h.

The results are most simply interpreted in terms of a reaction sequence, as shown in Scheme 1, analogous to that suggested by Kropp *et al.* for reactions of alkyl and vinyl iodides.[11,12] However, we cannot rule out for the methanolysis a more complex mechanism, shown in Scheme 2, based on that proposed by Schuster and his colleagues for the photomethanolysis of (iodomethyl)naphthalene.[15] In such a process, the initial photodissociation of the iodide RI into $R^{\cdot}$ radicals and $I^{\cdot}$ atoms is followed by complexing of the $I^{\cdot}$ with an RI molecule to give a radical species $RI_2^{\cdot}$, which then reacts with MeOH to give ROMe. In our case the attachment of the OMe group would have to follow dissociation of the complex to give a cation in order to account for the rearrangements observed.

Applications in Synthesis.—The photocatalysed reaction of $TsiSiPh_2I$ with MeOH to give $TsiSiPh_2OMe$, albeit as the minor product, offers the only available route to this compound at present, and no doubt the method could be extended to the preparation of other $TsiSiPh_2OR$ species.

$$\equiv SiI^{\cdot} \xrightarrow{h\nu} \equiv Si^{\cdot} + I^{\cdot}$$
$$\equiv SiI + I^{\cdot} \longrightarrow \equiv Si{-}I_2^{\cdot}$$
$$\equiv Si{-}I_2^{\cdot} \longrightarrow \equiv Si^{+} + I_2^{\dot{-}}$$
$$\equiv Si^{+} + MeOH \longrightarrow \equiv SiOMe + H^{+}$$
$$\equiv Si^{\cdot} + I^{\cdot} \longrightarrow \equiv SiI$$
$$\equiv Si^{\cdot} + I_2^{\dot{-}} \longrightarrow \equiv SiI + I^{-}$$

Scheme 2.

Irradiation of $TsiSiPh_2I$ in anisole offers a much better route to the cyclic species (6) than the pyrolysis by which this was previously made,[5] and prolonged irradiation in other solvents might give even better results.

The photocatalysed formation of the anilide (5) offers an alternative to the use of the perchlorate $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OClO_3)$, which would probably give (5) on treatment with aniline (*cf.* ref. 7).

Experimental

Materials.—The preparations of $TsiSiPh_2I$, TsiSiPhMeI, and $TsiSiMe_2I$ have been described previously.[1]

Methanol was dried by treatment with $Mg(OMe)_2$ and distillation from the latter. The other solvents were used as supplied.

Irradiations.—The quartz reaction vessel was irradiated from a distance of 10 cm with a Hanovia medium-pressure mercury lamp, model U.V.S. 500. The mixture was magnetically stirred throughout, and a nitrogen atmosphere was maintained unless otherwise indicated.

U.v. Spectra.—The u.v. spectra in cyclohexane of the silicon iodides used were as follows: (a) $TsiSiMe_2I$; a tail from *ca.* 400 nm then a sharp rise in absorption beginning at *ca.* 263 nm (ε 118), with ε 690 at 233 nm, 1 710 at 227 nm, and a flat maximum at 217 nm (ε 2 550); (b) $TsiSiPh_2I$; a tail from *ca.* 330 nm, then a sharp rise beginning at *ca.* 295 nm (ε 70), with shoulders at 274 (ε 1 060), 267 (1 610), and 222 nm (16 300); (c) TsiSiPhMeI; a tail from *ca.* 330 nm, then a sharp rise beginning at *ca.* 280 nm (ε 100), with shoulders at 274 (ε 380), 267 (550), and 261 nm (620), with a flat maximum at 220 nm (ε 10 000).

Product Compositions.—After the irradiation of solutions of stirred suspensions (in MeOH or $PhNH_2$) or solutions (in the other solvents) of (1a) the organosilicon mixture was isolated by evaporation of the solvent, sometimes after initial extraction into hexane (see below). It was taken up in CCl_4, and the ^1H n.m.r. spectrum was recorded. The composition was determined by comparing the integrated signals from the relevant Me_3Si peaks with that from the aromatic protons. For example, for mixtures of (1a), (2a), and (2b), the integrated signals from the Me_3Si groups at δ 0.40, 0.24, and 0.21, respectively, were compared with those from all the phenyl groups. [Authentic samples of (1b), (2a), (2b), (3), (4), and (6) were available for comparison,[1,3,5] and a pure sample of (5) was obtained from the irradiation as described below.] The uncertainty in the results arises from overlap of the MeSi peaks from small amounts of unidentified products.

Reactions of (1a) *in* MeOH.—After the irradiation of a suspension of (1a) (usually 0.1—0.5 g) in MeOH (10 cm^3) the product mixture was isolated either by evaporation of the solvent under reduced pressure (Procedure A) or by addition of hexane and washing with water, followed by separation, drying, and evaporation of the organic layer (Procedure B). For determination of the ^1H n.m.r. spectrum the residue was taken up in CCl_4 containing a little CH_2Cl_2 to act as a reference and lock. Procedure A was used for samples withdrawn before the final reaction time listed in the Table, and procedure B for work-up of the whole remaining mixture after the full reaction time.

Additional features are noted below.

(a) After a 1 h irradiation of a suspension of (1a) (0.7 g) in 0.1M-NaOMe in MeOH (40 cm^3), work-up was by Procedure B. The mixture was separated by preparative t.l.c. (SiO_2, hexane) into (2a), (2b), and an unidentified product (possibly a mixture) showing ^1H n.m.r. singlets at δ −0.01, 0.03, 0.22, 0.27, 0.43, and 0.48, and a multiplet at 7.0—8.0. This product accounted for a high proportion of the unidentified material in this reaction, and was also present, to a lesser extent, in the products from the other irradiations in MeOH.

(b) In an experiment additional to that referred to in the Table, O_2 was bubbled through a stirred suspension of (1a) (0.2 g) in MeOH (10 cm^3). After 1 h a sample was removed and evaporated to dryness. The ^1H n.m.r. spectrum revealed that in addition to the peaks from (1a), (2a), and (2b) there was a fairly prominent peak at δ 0.52, two small peaks at δ 1.19 and 1.29, and an extra peak in the OMe region at δ 3.48. After 4 h the peaks at δ 0.52, 1.19, and 1.29 had disappeared, while the peaks at δ 3.52 ($TsiSiPh_2O$*Me*) and 3.48 were enhanced.

(c) A suspension of (1a) (0.5 g) in 3M-$LiNO_3$ in MeOH (20 cm^3) was irradiated for 3 h. Work-up by Procedure B left a residue which showed bands at 1 590 and 1 285 cm^{-1} in the i.r. spectrum identical to those given by the nitrate (3).[3] Analysis by ^1H n.m.r. spectroscopy indicated that (1a), (2a), (2b), and (3) were present in the proportions shown in the Table.

Reaction of (1a) *with* $PhNH_2$.—A mixture of (1a) (0.50 g) and aniline (10 cm^3) was irradiated for 8 h, then added to hexane. After several washings with water, the organic layer was separated and the solvent evaporated off. The ^1H n.m.r. spectrum of the residue showed that it was very predominantly the rearranged anilide (5), and that no unchanged (1a) remained. The product was purified by t.l.c. (SiO_2; 80 : 20 v/v n-C_6H_{14}–$CHCl_3$), and recrystallization from MeOH gave *bis(trimethylsilyl)(methyldiphenylsilyl)[dimethyl(phenylamino)-silyl]methane* (5), m.p. 129 °C, δ(CCl_4) 0.27 (18 H, s, $SiMe_3$), 0.47 (6 H, s, $SiMe_2$), 1.03 (3 H, s, SiMe), 3.8br (1 H, s, NH), and 6.2—8.1 (15 H, m, aryl-H) (Found: C, 66.4; H, 8.7; N, 2.8. $C_{24}H_{43}NSi_4$ requires C, 66.5; H, 8.5; N, 2.8%).

Reactions of (1a) *in Other Media*.—(a) A solution of (1a) (0.2 g) in n-pentane (10 cm^3) was irradiated, and samples (1 cm^3) were removed at various times and evaporated to dryness under reduced pressure. The ^1H n.m.r. spectrum showed the presence of starting material, rearranged iodide (1b), and unidentified products. The approximate percentages of (1a) and (1b) in the products were 26 and 37 after 2 h, 21 and 37 after 4 h, and 18 and 41 after 6 h.

(b) Reaction in n-hexane for 2 h gave (1a) (30%) and (1b) (48%) and the same additional products as in pentane. When O_2 was bubbled through the solution during irradiation, the ^1H n.m.r. spectrum was complex but it could be established that no (1a) or (1b) was present. An unassigned peak at δ 0.28 was prominent.

(c) A solution of (1a) (0.2 g) in benzene (10 cm^3) was irradiated. After 2 h a sample (1 cm^3) was removed and the solvent evaporated off under reduced pressure. The ^1H n.m.r. spectrum showed the presence of (1a) (30%) and (1b) (39%), and numerous other peaks mainly corresponding to those arising from the reactions in pentane or hexane, but with an additional peak at δ 0.22. After 4 h irradiation, (1a) (19%) and (1b) (34%) were present and the peak at δ 0.22 [which does not correspond with a peak of compound (6)] was enhanced.

(d) The recovered product mixture from the reaction of (1a) in Et_2O for 3 h contained (1a) (19%) and (1b) (31%), and gave no ^1H n.m.r. peaks in the OEt region.

(e) A solution of (1a) (0.2 g) in PhOMe (10 cm^3) was irradiated and samples (1 cm^3) were withdrawn at intervals and evaporated. After 1 h, (1a) (27%), (1b) (47%), and several unidentified materials were present. After 4 h only 28% of (1b) was present, and after 9 h only 4%. The ^1H n.m.r. spectrum after this time showed the presence of three small singlets in the OMe region presumably arising from small amounts of anisole derivatives. The irradiation was continued for 29 h, after which g.l.c. showed the presence of several components, the main product being (6). This was isolated by preparative t.l.c. (SiO_2; 20 : 80 v/v $CHCl_3$–n-hexane) and shown to be identical with an authentic sample.[5] The peaks at δ −0.21 and 0.19 due to (6) were prominent in the ^1H n.m.r. spectrum of the product mixture after 9 and 29 h.

When a solution of (1a) (0.2 g) in PhOMe (10 cm^3) was refluxed for 9 h, evaporation of the solvent gave exclusively unchanged (1a).

(f) A solution of (1a) (0.5 g) in CCl_4 (10 cm^3) was irradiated for 2 h, during which a dark brown colour developed. Evaporation of a sample gave crystals of iodine, so methanol was added to the main bulk and the mixture shaken with aqueous sodium thiosulphate then with water. Evaporation of the organic layer gave a residue with a complex ^1H n.m.r. spectrum, and a mass spectrum indicating that (1a) and the corresponding chloride (4) (and/or its rearranged isomer) were present. G.l.c. (2 m, 5% OV101 on 100—120 mesh Chromosorb at 220 °C) showed the presence of three components A—C (in order of increasing retention time), in an approximate ratio of 24 : 13 : 63. These were separated by preparative g.l.c. (2 m, 20% OV101 CO 999 on 80—100 mesh Chromosorb P at 250 °C). Component A [δ (with relative integrations) −0.05 (s, 58), 0.06 (s, 13), 0.48 (s, 22), 0.88 (s, 6), and 7.2—7.9 (m, 43); *m/e* 73 (68%), 135 (100), 175 (20), 185 (22), 197 (45), 246 (44), 390 (60), and 407 (3)] was not identified, but it was not the rearranged chloride $(Me_3Si)_2C(SiPh_2Me)(SiMe_2Cl)$. Component B was unrearranged chloride, and C was unchanged (1a).

Reaction of TsiSiPhMeI *in n-Pentane*.—A solution of TsiSiPhMeI (0.2 g) in n-pentane (10 cm^3) was irradiated and samples (1 cm^3) were withdrawn at intervals. After 1 h, along with unidentified materials, the unchanged starting material (67%) and its rearranged isomer $(Me_3Si)_2C(SiPh_2Me)(SiMe_2I)$ (21%) were present, and the proportions fell to 43 and 32% after 2 h, and <5 and 45% after 4 h.

Reaction of $TsiSiMe_2I$ *with* MeOH.—(a) A suspension of $TsiSiMe_2I$ (0.2 g) in MeOH (10 cm^3) (not all the iodide was initially in solution) was irradiated and samples (1 cm^3) were withdrawn at intervals and evaporated under reduced pressure. The ^1H n.m.r. spectrum showed that the residue in all cases consisted of $TsiSiMe_2I$ and $TsiSiMe_2OMe$ only, and their ratios after various times were: 1 h, 75 : 25, 2 h, 45 : 55; 8 h, 35 : 65; 14 h, 20 : 80; 20 h, 15 : 85.

(b) A solution of $TsiSiMe_2I$ (0.2 g) in benzene (3 cm^3) was diluted with MeOH (7 cm^3). The solution was irradiated for

8 h then evaporated under reduced pressure. The residue was shown by ^1H n.m.r. spectroscopy to consist of $TsiSiMe_2I$ and $TsiSiMe_2OMe$ in 38 : 62 ratio.

Irradiation of $TsiSiPh_2Br$ *in* MeOH.—A mixture of $TsiSiPh_2Br$ (0.2 g) and MeOH (10 cm^3) was irradiated for 5 h. Evaporation gave exclusively unchanged $TsiSiPh_2Br$.

References

1 S. S. Dua, C. Eaborn, D. A. R. Happer, S. P. Hopper, K. D. Safa, and D. R. M. Walton, *J. Organomet. Chem.*, 1979, **178**, 75.

2 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.

3 C. Eaborn, D. A. R. Happer, S. P. Hopper, and K. D. Safa, *J. Organomet. Chem.*, 1980, **188**, 179.

4 C. Eaborn, D. A. R. Happer, and K. D. Safa, *J. Organomet. Chem.*, 1980, **191**, 355.

5 C. Eaborn and K. D. Safa, *J. Organomet. Chem.*, 1980, **204**, 169.

6 C. Eaborn and F. M. S. Mahmoud, *J. Chem. Soc., Chem. Commun.*, 1981, 63; *J. Chem. Soc., Perkin Trans. 2*, 1981, **1309**.

7 C. Eaborn and F. M. S. Mahmoud, *J. Organomet. Chem.*, 1981, **220**, **139**.

8 C. Eaborn, K. D. Safa, A. Ritter, and W. Binder, *J. Chem. Soc., Chem. Commun.*, 1981, 175.

9 A. Al-Wassil and C. Eaborn, unpublished results.

10 B. J. Cornett, K. Y. Choo, and P. P. Gaspar, *J. Am. Chem. Soc.*, 1980, **102**, 377.

11 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.*, 1974, **96**, 7142; S. A. McNeeley and P. J. Kropp, *ibid.*, 1976, **98**, 4319; N. J. Pienta and P. J. Kropp, *ibid.*, 1978, **100**, 655.

12 P. J. Kropp, G. S. Poindexter, N. J. Pienta, and D. C. Hamilton, *J. Am. Chem. Soc.*, 1976, **98**, 8135.

13 H. Sakurai in ' Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, New York, 1973, vol. 2, ch. 25.

14 C. Eaborn, R. A. Jackson, and R. Pearce, *Chem. Commun.*, 1967, 920; S. W. Bennett, C. Eaborn, R. A. Jackson, and R. Pearce, *J. Organomet. Chem.*, 1971, **28**, 59.

15 G. B. Slocum, K. Kaufmann, and G. B. Schuster, *J. Am. Chem. Soc.*, 1981, **103**, 4625.

Received 26*th October* 1981; *Paper* 1/1658