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PYROLYSIS OF THE "TRISYL" COMPOUNDS $(Me_3Si)_3CSiPh_2I$ AND $(Me_3Si)_3CSiPhMeI$ *

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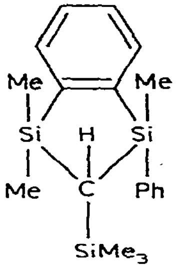
Summary

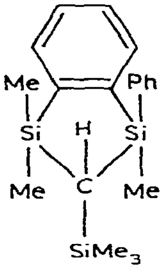
The compounds $(Me_3Si)_3CSiPh_2I$ and $(Me_3Si)_3CSiPhMeI$ have been shown to decompose on heating with formation of various 1,3-disilaindane derivatives, probably via free radical intermediates.

Introduction

We previously presented the results of a study of the pyrolysis of the [tris(trimethylsilyl)methyl]silicon compound $TsiSiPh_2F$ (Tsi = trisyl = $(Me_3Si)_3C$), which was shown to give the five-membered ring species I—III (derivatives of 1,3-disilaindane), probably via an intermediate sila-olefin $(Me_3Si)_2C{=}SiPh_2$, formed by loss of Me_3SiF [1]. We also reported that under similar conditions the corresponding chloride $TsiSiPh_2Cl$ underwent no decomposition. We have now found that the iodides $TsiSiPh_2I$ and $TsiSiPhMeI$ undergo pyrolysis readily to give 5-membered ring species with the same skeleton as I—III, but by a different type of route.



(I)



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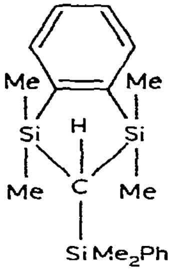

(III)

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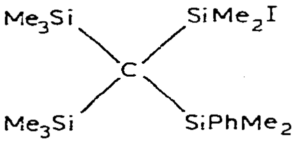
Results and discussion

Pyrolysis of TsiSiPhMeI

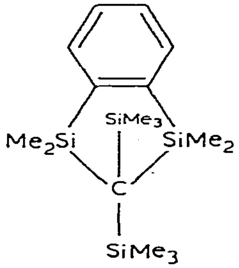
Although we studied TsiSiPh$_2$I before TsiSiPhMeI, we present the results for the latter first because of their relative simplicity.

. The TsiSiPhMeI was placed in a round-bottom flask fitted with a reflux condenser. A stream of nitrogen was passed through the flask which was gently heated with a Bunsen flame for 5 minutes. Rapid decomposition occurred and HI was evolved. (The average temperature of the molten material during the decomposition was estimated to be about 350°C. When the heating was carried out in a sealed tube at 260°C, about 55% of the starting material remained unchanged after 2 h.) The residue was recrystallized from methanol, and shown by TLC to contain 3 components, A, B, and C roughly in the ratio 10 : 80 : 10. These components were then separated by preparative TLC.

Product A gave a mass spectrum virtually identical with that of the original iodide, except for a small additional peak at *m/e* 371 which we suspect arises from an impurity. We believe that A has the structure IV. Compound IV is also formed by photolysis of TsiSiPhMeI [2], and gives peaks in the ^{1}H NMR spectrum at the same positions as those given by A, but A has an additional small peak at δ 1.38 ppm, probably due to impurity, and the integration ratios are not quite correct, possibly because the impurity also contributes to the peak at δ 0.34 ppm attributed to the protons of the (Me$_3$Si)$_2$C entity.



IV (? A)



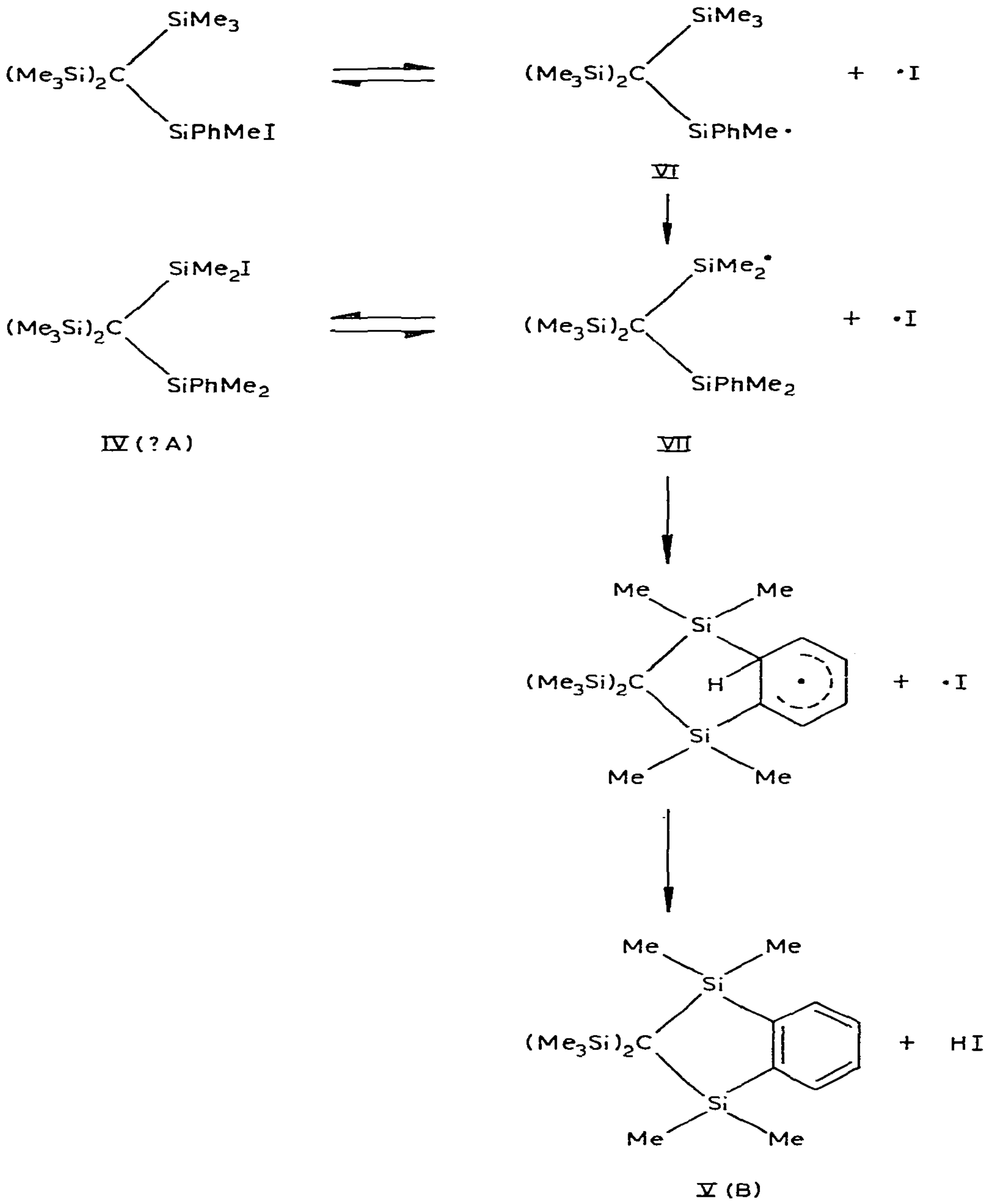
V (B)

The major product, B, was identified as V on the basis of its ^{1}H NMR and mass spectra. The third component, C, gave a complex ^{1}H NMR spectrum; GLC showed it to contain at least 5 species, and so it was not further investigated.

The simplest mechanism consistent with the results is shown in Scheme 1. This involves initial homolytic dissociation of the original iodide into a radical VI and an iodine atom. Radical VI then rearranges to radical VII, and the latter either recaptures the iodine atom to give the rearranged iodide IV or, by a free-radical aromatic substitution, ring-closes to give the product V (B); since HI is formed, the displaced H atom is presumably taken by the iodine atom. The rearranged iodide IV would also be expected to dissociate to give the radical VII, and some of the product V could have been formed via IV.

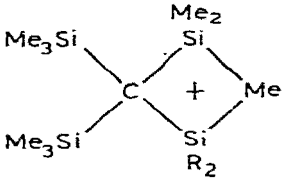
We have previously postulated the existence of bridged cations, of the form VIII, to account for rearrangements which occur during reactions of the iodides TsiSiR$_2$I with electrophiles in solution [3], and the possibility had to be considered that the dissociation of the iodides (Me$_3$Si)$_3$SiPhMeI and (Me$_3$Si)$_2$C-

SCHEME 1
PYROLYSIS OF TsiSiPhMeI

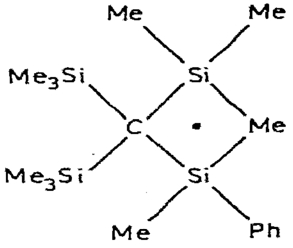


$(SiPhMe_2)(SiMe_2I)$ might give the analogous bridged radical, IX, although this would have to be in equilibrium with some (possibly very small amount) of the open radical VII for formation of the 5-membered ring species V to occur by a free radical aromatic substitution. This possibility seems to be excluded, however, by the observation that the free radical produced from TsiSiMe$_2$H by UV irradiation of its solution in hexane containing di-t-butyl peroxide gives an ESR spectrum entirely consistent with the simple radical TsiSiMe$_2^{\bullet}$ [4].

It is likely that the organosilicon radicals and the iodine atom largely remain associated as a radical pair within a solvent cage throughout the various transformations, all of which we assume to take place very rapidly following the initial dissociation.

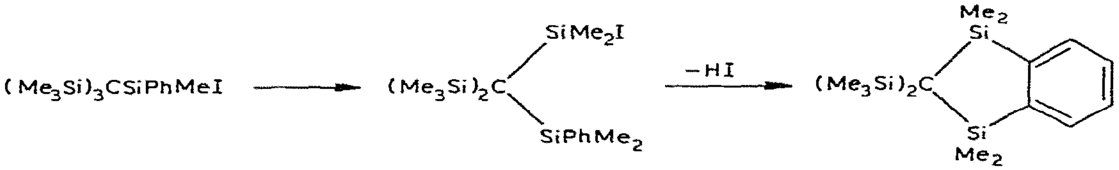


VIII



IX

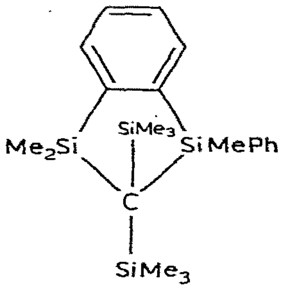
We cannot rule out the possibility that while the rearrangements involve free radical intermediates, the ring closures are molecular processes; e.g.,



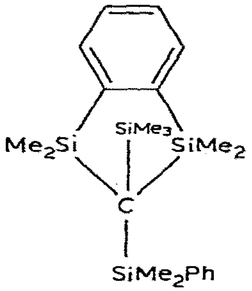
Pyrolysis of TsiSiPh$_2$I

The TsiSiPh$_2$I was also heated for 5 min with a flame beneath a reflux condenser in a round bottom flask and volatile material was carried off in a stream of nitrogen; the mean temperature of the mass during the decomposition is again estimated to be about 350° C. Benzene was collected in a cold trap and hydrogen iodide was absorbed in water. The fuming residue was recrystallized from methanol, and the recovered solid subjected to GLC to show four components D, E, F, and G, in ratios of approximately 40 : 3 : 27 : 30, and these were separated by preparative GLC. Component D was shown to contain 3 species, D1, D2, and D3, in approximately 1 : 2.5 : 1 ratio, and these were separated by TLC.

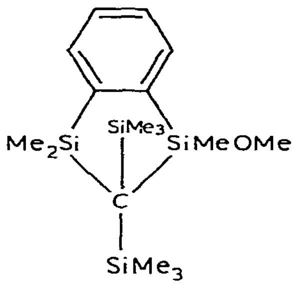
The product F was identified from its mass and ^{1}H NMR spectra as X, the analogue of the product V (B) from TsiSiPhMeI. Product G, which gave a mass spectrum virtually identical to that of F, but a different ^{1}H NMR spectrum, was judged to be the isomeric species XI. These products can be accounted for, as shown in Schemes 2a and 2b, by processes analogous to those in Scheme 1 but with the additional feature of migration of a Ph group within a radical.



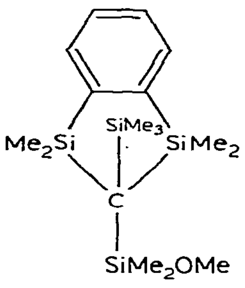
X



XI



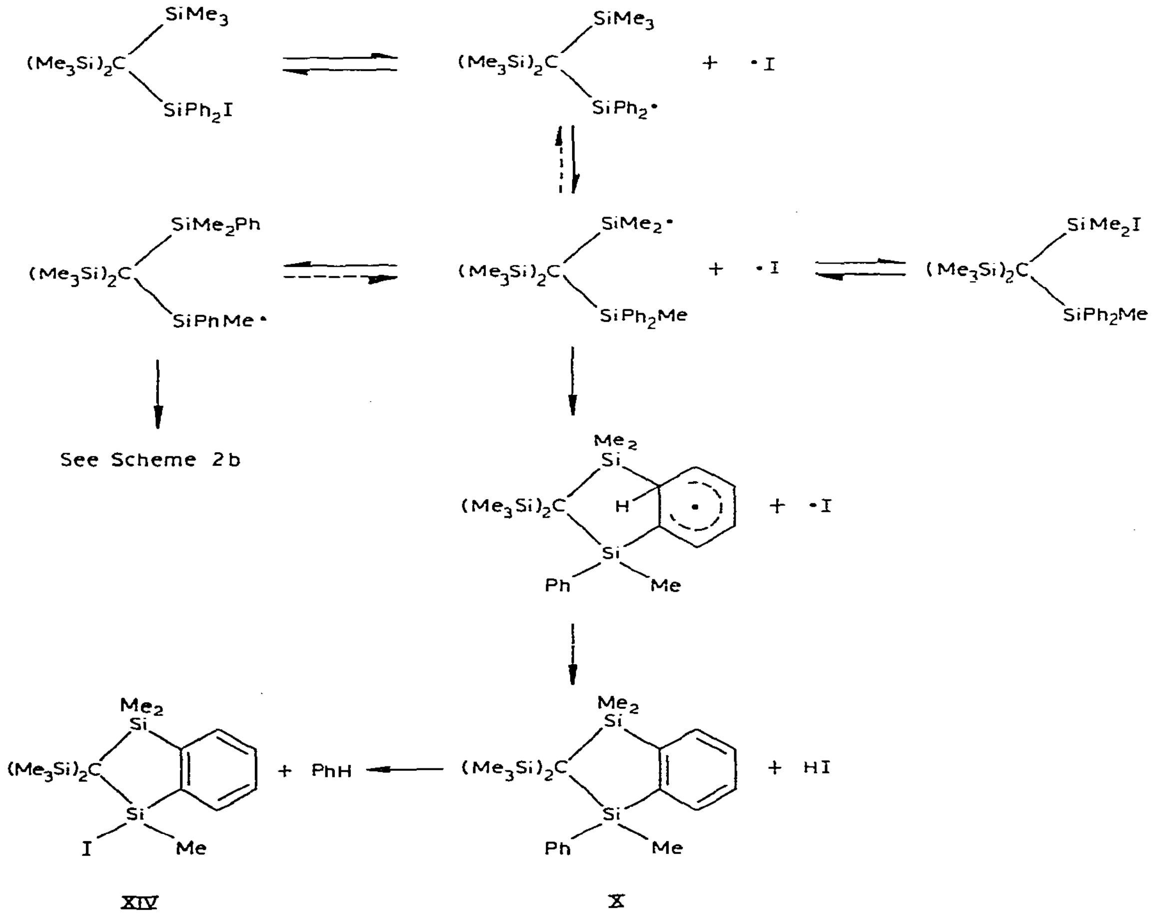
XII



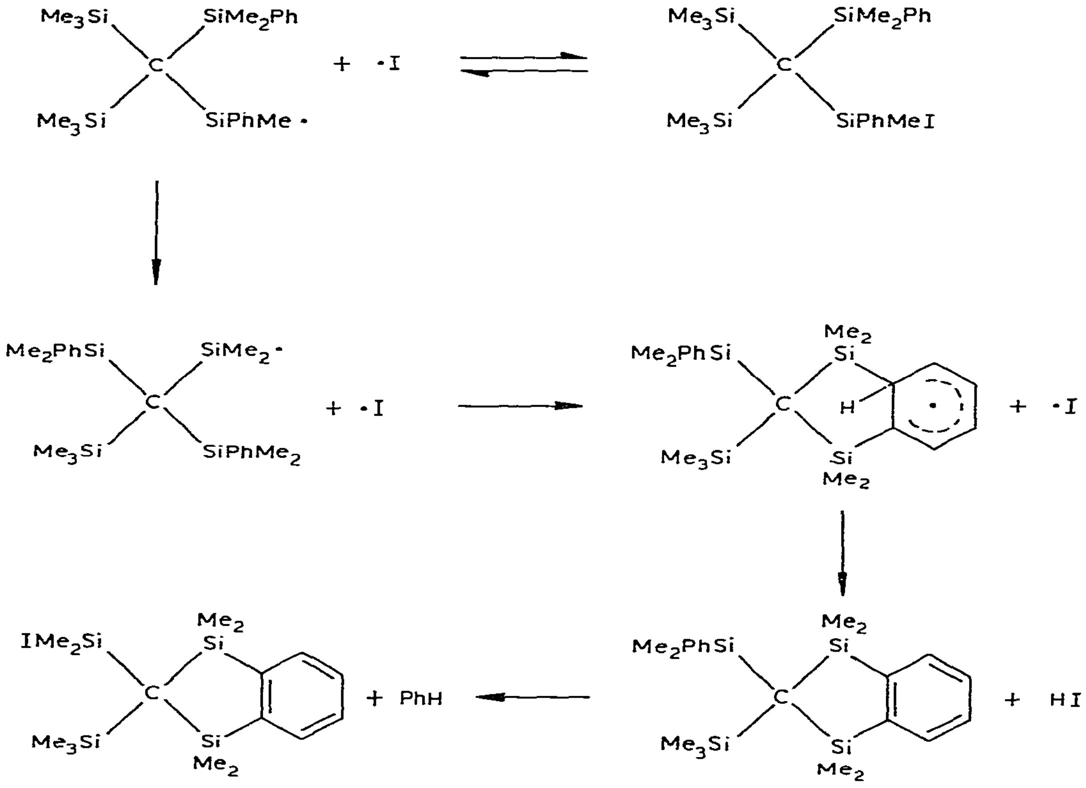
XIII

The products D1 and D2 were then identified from their ^{1}H NMR and mass spectra as the methoxides XII and XIII produced by methanolysis of the iodides XIV and XV formed from X and XI, respectively, by cleavage of the Si—Ph bond by HI. The evolution of benzene is thus accounted for.

SCHEME 2a
PYROLYSIS OF $TsiSiPh_2I$. POSSIBLE ROUTE TO PRODUCTS X AND XIV



SCHEME 2b
PYROLYSIS OF $TsiSiPh_2I$. POSSIBLE ROUTE TO PRODUCTS XI AND XV



XV

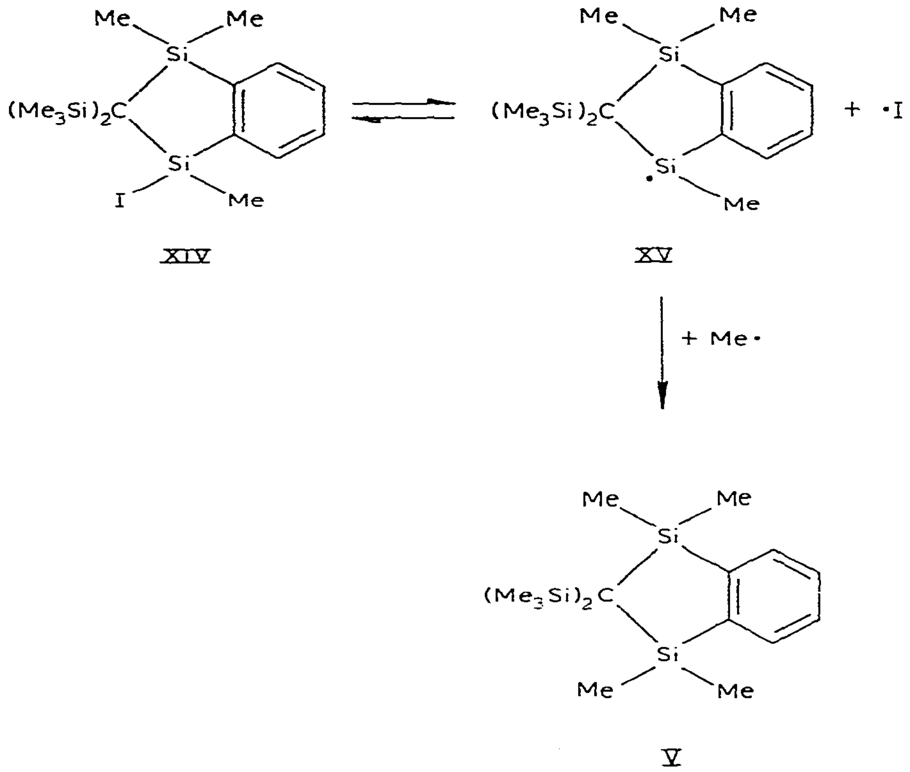
XI

Product D3 seems to consist mainly of compound V, which was obtained as product B from pyrolysis of TsiSiPhMeI. The mass spectrum of D3 was virtually identical with that of B, and the positions of the singlets from $SiMe_2$ and $SiMe_3$ groups and of the multiplets from the aryl proton were identical in the ^1H NMR spectra of the two samples. However, while for D3 the integration ratio for the $SiMe_3$ and $SiMe_2$ protons was as expected, the ratio of aryl protons to total SiMe protons was low, and the melting point of D3 (175—176°C) was also significantly lower than that of B (190—192°C). We think it highly likely that D3 consists mainly of V, but with some impurity giving rise to signals in the Me_2Si and Me_3Si regions overlapping with those of V.

The formation from $TsiSiPh_2I$ of V (in very small amount) requires an intermediate methyl transfer at some stage. One possibility, for example, shown in Scheme 3, is that some of the iodide XIV, produced by cleavage of X by HI, gives the radical XV, which abstracts a Me group from another molecule. A similar scheme can be written starting from XI.

Samples of $TsiSiPh_2I$ were also pyrolysed by heating in sealed tubes at 260°C. Roughly 55% of the starting material remained after 2 h and 10% after 4 h. The pattern of peaks in the ^1H NMR spectrum of the product mixture obtained after 4 h was very similar to that in the spectrum of the product mixture

SCHEME 3
PYROLYSIS OF TsiSiPh$_2$I. POSSIBLE ROUTE TO PRODUCT V



from heating with a flame for 5 min (though the relative heights of the peaks were different), but after 24 h at 260°C the Me$_3$Si peaks at δ −0.21 and −0.40 ppm had disappeared. These peaks arise from products X (F) and XI (G), and it is likely that the aryl—Ph bonds of these products are completely cleaved under the sealed tube conditions in which the HI is held in the system.

A final feature of interest is that the iodides XIV and XV must be reactive towards MeOH, even though they resemble the unreactive iodides of the type TsiSiPh$_2$I in having the iodine atom attached to a silicon atom which is joined to a carbon atom bearing three SiMe$_2$R groups. Presumably there is much less steric hindrance to nucleophilic substitution when some of the bonds are tied back in 5-membered rings. It is known, for example, that in the compounds I and II the exocyclic Me$_3$Si—CH—SiMe$_3$ angles are ca. 120°C.

Experimental

Spectra. The ^{1}H NMR spectra were recorded at 90 MHz with solutions in CCl$_4$ containing CH$_2$Cl$_2$ as reference; δ values are in ppm. Mass spectra were recorded at 70 eV.

Starting materials. The compounds TsiSiPh$_2$I and TsiSiPhMeI were prepared as previously described [5].

Pyrolysis of TsiSiPhMeI

(a) Heating with a flame. The TsiSiPhMeI (1.0 g) was placed in a 10 cm^3 round bottom flask fitted with a reflux water condenser and a nitrogen inlet. The nitrogen stream was led from the top of the condenser through a cold trap then into aqueous ammonia. The flask was heated gently with a Bunsen flame for about 5 min, during which much evident decomposition occurred, The aqueous ammonia was found to contain considerable amount of iodide ion, and it was assumed that HI had been evolved. The residue in the reaction flask was dissolved in MeOH then recovered by evaporation of the solvent at reduced pressure, the (solid) mixture was subjected to preparative TLC (silica gel; hexane) to give (in order of increasing distance from the base line) three components A, B, and C, in the rough ratios of 10 : 80 : 10.

Product A, had m.p. 224—226°C. Its mass spectrum showed the following main peaks (relative abundance in parentheses): (*m/e*) 463 (7), 371 (8), 351 (100), 335 (70), 263 (23), 247 (31), 201 (50), 175 (31), 135 (46), 73 (85); this spectrum is virtually identical with that of the starting iodide, except for the small additional peak at *m/e* 371 which is presumably due to an impurity. The ^{1}H NMR spectrum showed peaks, with relative integrations shown in parentheses, as follows: δ 0.34 (s, 28), 0.69 (s, 7), 1.02 (s, 7), 1.38 (s, 1.0), 7.2—7.9 (m, 8). The positions of the resonances at δ 0.34, 0.69, and 1.02 are consistent with the postulated structure $(Me_3Si)_2C(SiPh_2Me)(SiMe_2I)$, IV, but the integration ratio of Me_3Si/Me_2Si protons, (28/14 =) 2.0, is higher than the theoretical, (18/12 =) 1.5. The integration ratio for all SiMe to aryl protons, (43/8 =) 5.3 is fairly close to that expected, viz. (30/5 =) 6. It seems likely that the small peak at δ 1.38 is due to an impurity. The analysis was consistent with structure IV (Found: C, 42.8; H, 7.6: Calcd. for $C_{17}H_{35}ISi_4$: C, 42.7; H, 7.3%).

Product B had m.p. 190—192°C; *m/e* (with relative intensities in parentheses), 335 (100) ($M - Me$), 247 (53) ($M - Me - SiMe_4$), 175 (11), 73 (50) (Me_3Si); δ 0.11 (s, 18H, Me_3Si), 0.42 (s, 12H, Me_2Si); 7.1—7.6 (m, 4H, aryl-H). The multiplet at 7.1—7.6 had the expected symmetrical form. The analysis agreed with structure V (Found: C, 57.9; H, 9.8. Calcd. for $C_{17}H_{34}Si_4$; C, 58.3; H, 9.7%).

Product C gave a ^{1}H NMR spectrum showing 6 singlets in the Me_3Si region (δ 0.09, 0.13, 0.25, 0.36, 0.42 and 0.47) and three in the Me_2Si region, (δ 1.08, 1.42, and 1.91) but no signals in the aryl-H region. GLC gave 5 peaks, so the product was not further studied.

(b) Heating in a sealed tube. A sample of TsiSiPhMeI (50 mg) was sealed into a glass tube which was kept in a furnace at 260°C for 2 h. From the relative intensities of the aryl and $(Me_3Si)_3C$ proton signals in the ^{1}H NMR spectrum of the product mixture it was estimated that roughly 55% of the $(Me_3Si)_3CSiPhMeI$ remained. (No allowance was made for the conversion of some aryl—Si into aryl—H bonds.) The positions of all the significant peaks in the ^{1}H NMR spectrum coincided with those given by the product mixture from the heating with a flame for 5 min as described in (a) above, but the relative heights of the peaks differed in the two spectra.

Pyrolysis of TsiSiPh$_2$I

(a) Heating with flame. The pyrolysis of TsiSiPh$_2$I (6.0 g) was conducted

exactly as described above for TsiSiPhMeI. A substantial amount of benzene, which was identified by its smell and ^{1}H NMR spectrum, collected in the cold trap, and much iodide ion was detected in the aqueous ammonia trap. The fuming residue in the reaction flask was recrystallized from methanol, then subjected to analytical GLC, which gave 4 peaks corresponding in order of elution to components D, E, F, and G, with the peaks from F and G overlapped, in the approximate ratio 40 : 5 : 25 : 30. The components D, E, and combined F + G were isolated by preparative GLC (2 m, 20% OV101 on 80—100 mesh Chromosorb P with N_2 carrier gas at 260°C). Components F and G were then separated by preparative GLC on a different column (2 m, 20% Antarox 990 on 80—100 mesh Chromosorb P with N_2 as carrier gas at 250°C).

Examination by TLC showed that component D contained three species, D1, D2, and D3, in a ca. 1 : 2.5 : 1 ratio, and these were then separated by preparative TLC (SiO_2; hexane).

Product D1, which was assigned the structure XII (Found: C, 55.6; H, 9.5. Calcd. for $C_{17}H_{34}OSi_4$; C, 55.7; H, 9.3%), gave a mass spectrum as follows: *m/e* 351 (100) (*M* — Me), 247 (38) (*M* — Me — Me_3SiOMe), 175 (25), 73 (63). The ^{1}H NMR spectrum was as follows: δ 0.04 (s, 9H, Me_3Si), 0.18 (s, 9H, Me_3Si), 0.40 (s, 3H, 0.5 × Me_2Si), 0.44 (s, 3H, 0.5 × $SiMe_2$), 0.54 (s, 3H, Si*Me*OMe), 3.38 (s, 3H, OMe), 7.2—7.7 (m, 4H, aryl-H). The pattern of the aryl proton signals was similar to that in the *o*-phenylene bridged species. The two signals from the Me_2Si group arise from Me groups *cis* and *trans*, respectively, to the OMe group. This product formed about 9% of the overall product mixture from the pyrolysis.

Product D2 had m.p. 145—147°C, and gave a mass spectrum as follows: *m/e* 351 (100) (*M* — Me), 247 (45) (*M* — Me_3SiOMe — Me), 175 (22), 73 (22); thus the pattern was virtually identical with that of D1. The ^{1}H NMR spectrum was as follows: δ 0.11 (s, 15H), 0.42 (s, 6H), 0.44 (s, 6H, Si*Me*$_2$OMe), 3.36 (s, 3H, OMe) 7.2—7.6 (m, 4H, aryl-H). The structure XIII is assigned (Found: C, 55.7; H, 9.2. Calcd. for $C_{17}H_{34}OSi_4$; C, 55.7; H, 9.3%). The aryl multiplet had the expected symmetrical pattern. The peak at 0.11 is assumed to be due to the $SiMe_3$ plus half of the $SiMe_2$ protons, and that at 0.42 to the other half of the $SiMe_2$ protons, the splitting of the $SiMe_2$ resonances arising from Me groups *cis* and *trans*, respectively, to the $SiMe_2OMe$ groups. This compound constituted roughly 20% of the overall product mixture from the pyrolyses.

Product D3 had m.p. 175—176°C. Its mass spectrum, with peaks at *m/e* 335 (100), 247 (55), 175 (11) and 73 (50), was virtually identical with that of product B from TsiSiPhMeI. Its ^{1}H NMR spectrum was also identical with that of B, but the elemental analysis differed from that of B, and the product, which formed about 9% of the overall mixture from the pyrolysis, is thought to be impure V (Found: C, 56.9; H, 9.7. Calcd. for $C_{17}H_{34}Si_4$: C, 58.3; H, 9.7%).

Product E, m.p. 114—119°C, gave the following mass spectrum: *m/e* 527 (13), 381 (100), 293 (20), 263 (17), 175 (17), 73 (29). The ^{1}H NMR spectrum showed peaks at approximately δ —0.13 (s, rel. intensity 88), 0.07 (s, rel. intensity 31), 0.27 (s, rel. intensity 31), 0.47 (s, rel. intensity 10), 6.8—7.7 (m, rel. intensity 48). The aryl proton pattern was consistent with the presence of one bridging phenylene and one free phenyl group. The integration ratio for the peaks at 0.06, 0.27 and 0.47 are consistent with the presence of two identical

$SiMe_3$ groups (δ 0.06) and two sets of $SiMe_2Y$ groups (δ 0.27 and 0.47). This unidentified product formed only about 3% of the pyrolysis product mixture.

Compound F, which had m.p. 137°C, was assigned the structure X (Found: C, 63.6; H, 8.7. Calcd. for $C_{22}H_{36}Si_4$; C, 64.1; H, 8.7%). Its mass spectrum showed peaks as follows *m/e* 397 (100) (*M* — Me), 309 (33) (*M* — Me — $SiMe_4$), 247 (50) (*M* — $PhSiMe_3$ — Me), 135 (50), 73 (75). The ^{1}H NMR spectrum was consistent with X; δ, —0.21 (s, 9H, Me_3Si), 0.19 (s, 9H, Me_3Si), 0.42 (s, 3H, 0.5 × $SiMe_2$), 0.52 (s, 3H, 0.5 × Me_2Si), 0.75 (s, 3H, Si*Me*Ph), 7.1—7.7 (m, 9H, aryl-H). The aryl proton pattern was consistent with the presence of an *o*-phenylene bridge and a free Ph group. The splitting of the signal from the Me_2Si protons is due to the presence of Me groups *cis* and *trans*, respectively, to the Ph group. Product F formed about 30% of the pyrolysis product mixture.

Product G, which had m.p. 145—147°C, was assigned structure XI (Found: C, 63.6; H, 8.7. Calcd. for $C_{22}H_{36}Si_4$; C, 64.1; H, 8.7%). Its mass spectrum was very similar to that of F; *m/e* 397 (100), 309 (33), 247 (50), 135 (50), 73 (58). The ^{1}H NMR spectrum was consistent with structure XI; δ —0.40 (s, 9H, $SiMe_3$), 0.46 (s, 6H), 0.56 (s, 12H), 7.1—7.8 (s, 9H). The pattern for the aryl protons indicated that at least one *o*-phenylene bridge was present. The singlet at δ 0.46 is assumed to come from two Me groups at different intracyclic $SiMe_2$ centres, and that at 0.56 from the Si*Me*$_2$Ph and the other pair of Me groups on the intracyclic $SiMe_2$ centres, the chemical shift for Me groups *trans* to $SiMe_2Ph$ being different from those *cis* to the latter. Compound G represented about 30% of the pyrolysis product mixture.

(b) Heating in a metal bath. A sample of $TsiSiPh_2I$ (2 g) was placed in a round-bottom flask fitted as before, with the addition of a thermometer in the vapour space in the flask, and the flask was placed in a metal bath at 350°C. The mixture was refluxed as volatile material was carried off in the nitrogen stream. The temperature of the vapours above the decomposing liquid rose during 20 min to 180°C then stayed constant. Benzene was collected in the cold trap. After cooling, the fuming residue in the flask was treated with methanol. The recovered material gave a very complex ^{1}H NMR spectrum, showing all the peaks expected for the products noted in (a) above, plus several others, indicating that further secondary decomposition had occurred.

(c) Heating in a sealed tube. Samples (50 mg) contained in sealed tubes were treated in a furnace at 260°C for various times. After 2 h roughly 55% of the $TsiSiPh_2I$ remained unchanged. (The estimation was carried out as described for the reaction of TsiSiPhMeI.) After 4 h, about 10% remained. The ^{1}H NMR spectrum of the crude product mixture showed the same peaks as those given by the mixture obtained after the heating with a flame, as described under (a) above. After 24 h the peaks at δ —0.21 and —0.40 were absent.

Acknowledgements

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References

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. Organometal. Chem., 186 (1980) 309.

2 C. Eaborn and K.D. Safa, unpublished work.
3 C. Eaborn, D.A.R. Happer, S.P. Hopper and K.D. Safa, J. Organometal. Chem., 170 (1979) C9; 188 (1980) 179.
4 R.A. Jackson, personal communication.
5 S.S. Dua, C. Eaborn, D.A.R. Happer, S.P. Hopper, K.D. Safa and D.R.M. Walton, J. Organometal. Chem., 178 (1979) 75.