*Journal of Organometallic Chemistry*, 291 (1985) 25–33
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# REACTIONS OF $(Me_3Si)_3CSiMe_2R$ COMPOUNDS (R = $CH{=}CH_2$, $CH_2CH{=}CH_2$, $C{\equiv}CPh$, Ph, and $CH_2Ph$) WITH ELECTROPHILES

RAMADAN I. DAMJA, COLIN EABORN*, and WING-CHEONG SHAM
*School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)*

(Received February 10th, 1985)

## Summary

No products of addition to the multiple bond are formed in reactions of $TsiSiMe_2R$ species (Tsi = $(Me_3Si)_3C$; R = $CH{=}CH_2$, $CH_2CH{=}CH_2$, or ($C{\equiv}CPh$) with halogens or hydrogen halides. $TsiSiMe_2CH{=}CH_2$ gave (a) $TsiSiMe_2Cl$ on treatment with ICl in $CCl_4$; (b) $TsiSiMe_2Br$ on treatment with $Br_2$ in $CCl_4$; (c) $TsiSiMe_2I$ (slowly) on treatment with $I_2$ in $CCl_4$; and (d) $TsiSiMe_2OCOCF_3$ on treatment with neat $CF_3CO_2H$. $TsiSiMe_2CH_2CH{=}CH_2$ gave: (a) $TsiSiMe_2Cl$ and $TsiSiMe_2I$ on treatment with ICl in $CCl_4$; (b) $TsiSiMe_2Br$ on treatment with $Br_2$ in $CCl_4$; (c) $TsiSiMe_2I$ on treatment with $I_2$ in $CCl_4$; and (d) $TsiSiMe_2OCOCF_3$ rapidly on treatment with neat $CF_3CO_2H$. $TsiSiMe_2Ph$ gave $TsiSiMe_2Br$ on treatment with $Br_2$ in $CCl_4$ or $CH_3CO_2H$, and (b) $TsiSiMe_2Cl$ on treatment with HCl in $Et_2O$. Reaction of $TsiSiMe_2Ph$ with nitric acid in $(CH_3CO)_2O$ gave two mono-nitration products, probably the *m*- and *p*-isomers. Reaction of $TsiSiMe_2CH_2Ph$ with $Br_2$ gave exclusively $TsiSiMe_2Br$, whereas reaction with nitric acid in $(CH_3CO)_2O$ gave *o*- and *p*-nitro derivatives in 65/35 ratio. This last result casts serious doubt on previously proposed explanations of the predominance of *ortho*-nitration in the case of $Me_3SiCH_2Ph$.

## Introduction

Much interesting chemistry has emerged from studies of tris(trimethylsilyl)methyl ('trisyl') derivatives of the type $TsiSiR_2X$ (Tsi = $(Me_3Si)_3C$) in which there is severe inhibition by steric hindrance to attack at the functional silicon centre [1]. We thus decided to study the reactions with electrophiles of the compounds $TsiSiMe_2R$, where R = $CH{=}CH_2$, $CH_2CH{=}CH_2$, $C{\equiv}CPh$, Ph, or $CH_2Ph$, in order to find out whether they would show unusual features.

The interest in the compounds with R = $CH{=}CH_2$, $CH_2CH{=}CH_2$, or $C{\equiv}CPh$, lay in the possibility that addition to the multiple bonds might occur, to give species for further study. In the case of reactions of the corresponding $Me_3SiR$ compounds

0022-328X/85/$03.30

with, e.g. halogens, $X_2$, or hydrogen halides, HX, it is normally assumed that $X^+$ or $H^+$ first attaches to give a carbonium ion stabilized by the $\beta$-silyl group, e.g. $Me_3SiCH_2CH_2{}^+$, $Me_3SiCH_2\overset{+}{C}HCH_3$, and $Me_3SiCH{=}\overset{+}{C}HPh$, and that the nucleophile $X^-$ can then attack either at the carbonium ion centre to give the addition product, or at the silicon to give cleavage products (e.g. $Me_3SiX$ and $CH_2{=}CHCH_3$). With $TsiSiMe_2R$ inhibition of the attack at silicon might thus have diverted the reactions towards addition; in fact, as shown below, only cleavage occurred in all the cases examined.

The interest in $TsiSiMe_2CH_2Ph$ lay primarily in its reaction with $HNO_3/(CH_3CO)_2O$. Reaction of $Me_3SiCH_2Ph$ with this nitrating agent gives the *o*- and *p*-nitro derivatives in ca. 5.7/1 ratio [2,3], and nitration with copper nitrate in $(CH_3CO)_2O$ gives these isomers in ca. 4/1 ratio [4]. The surprising predominance of the *ortho*-nitro product (the *ortho*-position of $Me_3SiCH_2Ph$ is 9 times less reactive than the *para*- in hydrogen exchange [5], and parallel behaviour is observed in acid-cleavage of *o*- and *p*-$Me_3SiCH_2C_6H_4SiMe_3$ [6]) has been attributed to coordination to silicon of a nucleophilic centre of the nitrating agent (e.g. an O atom of $NO_2{}^+$ [3] or in the incipient $NO_3{}^-$ ion in $N_2O_5$ [6]), and if this were the correct explanation then no such effect should be observed with $TsiSiMe_2CH_2Ph$ because of the great steric hindrance to additional coordination at the relevant Si atom.

## Results and discussion

### *Preparation of TsiSiMe₂R compounds*

The required compounds were obtained by reaction of TsiLi * with (a) $Me_2Si(CH{=}CH_2)Cl$, (b) $Me_2Si(CH_2CH{=}CH_2)Cl$, (c) $Me_2Si(C{\equiv}CPh)F$, or (d) $Me_2Si(CH_2Ph)F$.

### *Reactions of TsiSiMe₂R (R = CH=CH₂, CH₂CH=CH₂, or C≡CPh)*

(i) The vinyl compound $TsiSiMe_2CH{=}CH_2$ was found not to react with an equimolar amount of ICl in $CCl_4$ during 10 d at room temperature, but when an excess of ICl (and thus a higher concentration of the reagent, which is probably important because this type of reaction is likely to be of high order in the halogen) was used, complete conversion into $TsiSiMe_2Cl$ had taken place by the time the first $^1H$ NMR spectrum could be recorded (i.e. within 1 min). Subsequently $(Me_3Si)_2C(SiMe_2Cl)_2$, $Me_3SiC(SiMe_2Cl)_3$, and $C(SiMe_2Cl)_4$ were successively formed. (Similar successive cleavages were noted when $(Me_3Si)_4C$ was treated with ICl, but the cleavage of the first Si–C bond was slower than in the case of the vinyl compound [8].) Similar behaviour was observed in the reaction of $TsiSiMe_2CH{=}CH_2$ with IBr in $CCl_4$; i.e. no reaction with an equivalent amount of IBr, but very rapid reaction to give $TsiSiMe_2Br$ when excess of the latter was used, followed by successive formation of $(Me_3Si)_2C(SiMe_2Br)_2$, $(Me_3Si)C(SiMe_2Br)_3$, and $C(SiMe_2Br)_4$.

Reaction of $TsiSiMe_2CH{=}CH_2$ with an excess of $Br_2$ in refluxing $CCl_4$ was complete within 3 h, and the organosilicon product was exclusively $TsiSiMe_2Br$. No

---

* For convenience we represent the organolithium reagent formed from TsiH and MeLi in THF (tetrahydrofuran) as TsiLi, although the actual structure is $[Li(THF)_4][Li(Tsi)_2]$ [7].

further reaction took place on prolonged reflux. Reaction with excess of $I_2$ in $CCl_4$ was much slower, and required about 5 d under reflux for completion; the organosilicon product was exclusively $TsiSiMe_2I$.

No reactions occurred when HCl or HBr was passed into a refluxing solution of $TsiSiMe_2CH=CH_2$ in $CCl_4$. The reaction of $TsiSiMe_2CH=CH_2$ with neat $CF_3CO_2H$ at room temperature was quite slow, and 3 d were required for complete reaction. The organosilicon product was exclusively $TsiSiMe_2OCOCF_3$.

(ii) The reaction of the allyl compound $TsiSiMe_2CH_2CH=CH_2$ with a one molar equivalent of $I_2$ in $CCl_4$ at room temperature was ca. 55% complete in 23 h, and complete after 4 d; the product was $TsiSiMe_2I$. Reactions with $Br_2$ under similar conditions was somewhat faster, being 55% complete in 5 h and complete within 1 d; the product was $TsiSiMe_2Br$. The reaction with one molar equivalent of ICl was initially even faster; after 1 h at room temperature $TsiSiMe_2I$, $TsiSiMe_2Cl$, and $TsiSiMe_2CH_2CH=CH_2$ were present in 5/11/8 ratio, but there was no significant change in a further 6 h, presumably because ICl not used up in the cleavage had reacted with $CH_2=CHCH_2I$.

The reaction of $TsiSiMe_2CH_2CH=CH_2$ with $I_2$ was repeated at −70°C with $Et_2O$ as solvent because of the possibility that an addition product might be preferentially formed under these conditions, but after 7 h the $^1H$ NMR spectrum recorded at room temperature showed that $TsiSiMe_2I$ was the only product.

No reaction occurred when HCl or HBr was bubbled through a solution of $TsiSiMe_2CH_2CH=CH_2$ in $Et_2O$ at either −70 or 0°C, or when HI was bubbled through a solution in $Et_2O$ at −70°C and the mixture was subsequently allowed to warm to room temperature.

Complete cleavage, to give $TsiSiMe_2OCOCF_3$, occurred when a solution of $TsiSiMe_2CH_2CH=CH_2$ in neat $CF_3CO_2H$ was kept for 30 min at room temperature.

(iii) No reaction occurred between $TsiSiMe_2C{\equiv}CPh$ and $I_2$ in $CCl_4$ during 12 d at room temperature. Reaction with an equimolar amount of $Br_2$ in $CCl_4$ was only about 25% complete after 7 d at room temperature; the product was $TsiSiMe_2Br$. With 4 molar equivalents of $Br_2$, the cleavage was complete within 0.5 h.

No reaction occurred when HCl was bubbled for 6 h through a solution of $TsiSiMe_2C{\equiv}CPh$ in $Et_2O$ at either −70 or 0°C. However, when the procedure was repeated at room temperature complete cleavage to $TsiSiMe_2Cl$ took place.

(iv) In none of the above reactions was addition to the multiple bond observed. Presumably the initial attachment of the electrophile to carbon produces a leaving group so good that ionization to give a Me-bridged silico-cation [1,2] occurs in preference to attachment of a nucleophile at carbon.

### *Reactions of $TsiSiMe_2Ph$*

When $TsiSiMe_2Ph$ was treated with nitric acid in $(CH_3CO)_2O$ at 0°C (conditions used for nitration of $Me_3SiPh$ [9]) the solid product was shown by its $^1H$ NMR spectrum to be a mixture; there were four peaks in the Si-Me region, two at $\delta$ 0.35 and 0.73 in 9/2 integration ratio, and the other two at $\delta$ 0.40 and 0.67 in the same ratio, indicating the presence of two $TsiSiMe_2R'$ species. Attempts to separate these by TLC were unsuccessful, but GLC/MS showed that the two components, present in ca. 3/1 ratio were both mono-nitro products, $TsiSiMe_2C_6H_4NO_2$. Since nitration of $Me_3SiPh$ under comparable conditions gives *o*-, *m*-, and *p*-nitro products in ca. 27/42/32 ratio [9], it seems likely that the two mono-nitro products we obtained were the *m*- and *p*-isomers, but we cannot suggest which of these predominated.

When $TsiSiMe_2Ph$ was treated with $Br_2$ in $CCl_4$ at 60°C reaction was slow, but $TsiSiMe_2Br$ was formed. Reaction in $CH_3CO_2H$ at 60°C was initially markedly faster, but slowed down after about 80% of reaction; reaction would no doubt be much faster, and go to completion, if a higher concentration of $Br_2$ were used.

### *Reactions of* $TsiSiMe_2CH_2Ph$

No detectable reaction occurred in 24 h when a solution containing 0.26 mmol of $TsiSiMe_2CH_2Ph$ and 1 mmol of $Br_2$ in 10 $cm^3$ of $CCl_4$ was kept at room temperature for 24 h. When the procedure was repeated but with only 2 $cm^3$ of $CCl_4$, reaction was complete within 20 min; this result illustrates the importance of the concentration of halogen in reactions such as this, which are of high order with respect to the halogen. The product appeared to be exclusively $TsiSiMe_2CH_2$-$C_6H_4Br$-*p*, but formation of a small amount ($< 5\%$) of the *o*-isomer would have escaped detection. The high reactivity of $TsiSiMe_2CH_2Ph$ is consistent with the large activation of the *para*-position of $Me_3SiCH_2Ph$ in electrophilic hydrogen exchange [5].

Reaction with nitric acid in $CH_3CO_2H$ at 0°C gave a mixture of two mono-nitro products; the minor component (35%) was $TsiSiMe_2CH_2C_6H_4NO_2$-*p*, and it can be confidently assumed that the other (65%) was the *ortho*-isomer since nitration of $Me_3SiCH_2Ph$ gives little, if any, *m*-nitro product [2–4]. It is extremely unlikely that there can be significant coordination of the nitrating species to silicon in this highly sterically hindered compound, and thus it also seems most improbable that the high proportion of *ortho*-product in nitration of $Me_3SiCH_2Ph$ originates in such an effect.

## Experimental

### *General*

The $^1H$ NMR spectra were recorded at 90 MHz with solutions in $CCl_4$ containing $CH_2Cl_2$ as reference. The IR spectra were recorded with Nujol mulls. Mass spectra (EI) were obtained at 70 eV. M.p's were determined with samples in sealed tubes.

Solutions of TsiLi were prepared as described in Ref. 10.

### *Preparations of* $TsiSiMe_2R$ *compounds*

#### *(a)* $R = CH{=}CH_2$

A solution of $CH_2{=}CHMgBr$ (0.44 mol) in THF (150 $cm^3$) was added dropwise to $Me_2SiCl_2$ (0.44 mol) in THF (50 $cm^3$). The mixture was subsequently stirred at room temperature for 3 h then an excess of n-pentane was added. The solution was decanted from the solid (which was washed with some additional pentane) and distilled. The distillate of b.p. 65–80°C was carefully fractionated in a spinning band column with xylene as a chaser, and the fraction (5 g) of b.p. 79–81°C was shown by its $^1H$ NMR spectrum to be a mixture of $Me_2Si(CH{=}CH_2)Cl$ (75%) ($\delta$ 0.80, SiMe) and $Me_2Si(CH{=}CH_2)_2$ (25%) ($\delta$ 0.15, SiMe).

Some of the above mixture (3 g; containing 0.018 mol of $Me_2Si(CH{=}CH_2)Cl$) in THF (10 $cm^3$) was added dropwise to a solution of TsiLi (0.018 mmol) in THF (31 $cm^3$). The mixture was subsequently refluxed for 2 h then the solid was filtered off and washed with a little THF. The solution and washings were treated with aqueous $NH_4Cl$, and the organic layer was washed, dried ($MgSO_4$) and evaporated. The residue was washed with MeOH (1 $cm^3$), and the solid formed was recrystallized from EtOH to give $TsiSiMe_2(CH{=}CH_2)$ (55%), m.p. > 325°C; $\delta$(H) 0.24 (s, 27H, $SiMe_3$), 0.29 (s, 6H, $SiMe_2$) and 5.4–7.0 ppm (m, 3H, $CH{=}CH_2$); $\nu$(C=C) 1649 $cm^{-1}$; $m/z$ 301 ($[M-Me]^+$) (Found: C, 52.7; H, 11.2. $C_{13}H_{36}Si_4$ calcd.: C, 53.1; H, 11.5%).

*(b) R = $CH_2CH{=}CH_2$*

The compound $Me_2Si(CH_2CH{=}CH_2)Cl$, b.p. 110°C/760 mmHg (lit. [11] b.p. 110°C/756 mmHg) was obtained in 28% yield from $Me_2SiCl_2$ and the Grignard reagent prepared from $CH_2{=}CHCH_2Br$ and Mg in $Et_2O$.

Some of the $Me_2Si(CH_2CH{=}CH_2)Cl$ (10.9 g, 0.081 mol) was added dropwise to a solution of TsiLi (0.027 mol) in THF (100 $cm^3$) during 30 min. The mixture was subsequently refluxed for 24 h then treated with aqueous $NH_4Cl$. The organic layer was separated, washed, dried ($MgSO_4$), and evaporated under reduced pressure to leave an oil. A little liquid was distilled from this at 90°C/0.1 mmHg, and the residue was sublimed (100°C/0.2 mmHg) to give $TsiSiMe_2(CH_2CH{=}CH_2)$ (3.4 g, 38% based on TsiLi used); m.p. 285°C; $\delta$(H) 0.23 (s, 6H, $SiMe_2$), 0.25 (s, 27H, $SiMe_3$), 1.76 (d, 2H, $CH_2$), and 5.6–6.1 ppm (m, 3H, $CH{=}CH_2$); $\nu$(C=C) 1635 $cm^{-1}$; $m/z$ 315 (10%; $[M-Me]^+$), 289 (90, $[M-CH_2CH{=}CH_2]^+$), 73 (100, $[SiMe_3]^+$) (Found: C, 54.2; H, 11.3, $C_{15}H_{38}Si_4$ calcd.: C, 54.4; H, 11.4%).

*(c) R = C≡CPh*

The chloride $Me_2Si(C{\equiv}CPh)Cl$ (34%), b.p. 125°C/10 mmHg, was prepared by a published method [12]. Some of it (27 g) was placed in a polyethylene vessel, and EtOH (100 $cm^3$) and 40% aqueous HF (40 g) were added [cf. ref. 13]. The mixture was stirred at room temperature for 7 h then added to an excess of light petroleum (b.p. 30–40°C). The organic layer was separated, washed with water several times, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was distilled to give $Me_2Si(C{\equiv}CPh)F$, b.p. 52°C/1 mmHg (lit. [12], b.p. 61°C/4 mmHg).

Some of the $Me_2Si(C{\equiv}CPh)F$ (6.0 g, 0.034 mol) was added dropwise to a solution of TsiLi (0.040 mol) in THF (120 $cm^3$). The mixture was refluxed for 18 h then the solvent was removed under vacuum. The residue was added cautiously to ice-cold aqueous $NH_4Cl$, and organic material was extracted with light petroleum, b.p. 40–60°C. The petroleum was evaporated off, and a little EtOH was added to the residue. The mixture was kept at −20°C overnight, and the white solid which separated was filtered off, washed with cold EtOH, then sublimed (115°C/0.1 mmHg) to give $TsiSiMe_2(C{\equiv}CPh)$ (2.1 g, 16%), m.p. 144°C; $\delta$(H) 0.36 (s, 27H, $SiMe_3$), 0.53 (s, 6H, $SiMe_2$), 7.3–7.5 ppm (m, 5H, $C_6H_5$); $\nu$(C≡C) 2150 $cm^{-1}$; $m/z$ 375 (90%, $[M-Me]^+$), 201 (15, $[M-Me_3SiC{\equiv}CPh-Me]^+$), and 73 (100, $[Me_3Si]^+$). (Found: C, 61.7; H, 9.7. $C_{20}H_{38}Si_4$ calcd.: C, 61.5; H, 9.7%).

*(d) R = Ph*

This was prepared as previously described [14].

*(e) R = $CH_2Ph$*

A solution of the Grignard reagent made from $PhCH_2Cl$ (130 g) and Mg (30 g) in $Et_2O$ (600 $cm^3$) was added dropwise to $Me_2SiCl_2$ (150 g) in $Et_2O$ (200 $cm^3$). The mixture was subsequently refluxed for 1 h, then an excess of 2 *M* aqueous hydrochloric acid was added cautiously with ice-cooling. The organic layer was separated, washed, and evaporated, and the residue was placed in a polyethylene vessel and treated with 45 g of 40% aqueous HF in EtOH (100 $cm^3$) (cf. ref. 13). The mixture was kept at 50°C for 6 h then cooled and added to an excess of water. Ether extraction following by washing, drying ($MgSO_4$), and evaporation left a residue, which was fractionated to give a good amount of $Me_2Si(CH_2Ph)F$, b.p. 82°C/30 mmHg (lit. [15], b.p. 183.5–184.5°C/760 mmHg).

Some of the fluoride (7.0 g, 0.042 mol) was added dropwise to a solution of TsiLi (0.025 mol) in THF (100 $cm^3$). The mixture was refluxed for 16 h then cooled and added to an excess of ice-cold aqueous $NH_4Cl$. The organic layer was washed, dried ($MgSO_4$), and evaporated under reduced pressure. Ethanol was added to the residue, and the mixture was kept overnight at −20°C. The solid which separated was filtered off, and sublimed (120°C/0.1 mmHg) to give $TsiSiMe_2(CH_2Ph)$ (1.95 g, 20%), m.p. 137.5°C; $\delta$(H) 0.14 (s, 6H, $SiMe_2$), 0.32 (s, 27H, $SiMe_3$), 2.31 (s, 2H, $CH_2$), and 6.9–7.2 ppm (m, 5H, $C_6H_5$); $m/z$ 365 (10; $[M-Me]^+$), 289 (100 $[M-CH_2Ph]^+$) (Found: C, 59.7; H, 10.8. $C_{19}H_{40}Si_4$ calcd.: C, 59.9; H, 10.5%).

*Reactions with electrophiles*

*(a) R = CH=CH$_2$ (I)*

(i) A solution of I (35 mg, 0.11 mmol) and $I_2$ (2.0 g, 7.9 mmol) in $CCl_4$ (20 $cm^3$) was refluxed and the $^1H$ NMR spectrum was recorded at intervals. Conversion into $TsiSiMe_2I$ ($\delta$ 1.08 (s, 6H) and 0.36 (s, 27H)) was complete within 5 d. The solution was shaken with aqueous $NaHSO_3$ to remove $I_2$, volatile material was removed under reduced pressure, and the residue shown to be exclusively $TsiSiMe_2I$ by comparison with an authentic sample.

(ii) A procedure similar to that in (i) was carried out with I (0.13 mmol) and $Br_2$ (0.18 mol) in $CCl_4$ (10 $cm^3$). Conversion into $TsiSiMe_2Br$ ($\delta$ 0.27 (s, 27H)) and 0.76 (s, 6H) was complete within 3 h. The solid isolated ($m/z$ 333, 355, $[M-Me]^+$) had properties identical with those of an authentic sample.

(iii) A 1 *M* solution of ICl (0.5 mmol) in $CCl_4$ (0.5 $cm^3$) was added to I (10 mg, 0.031 mmol) in an NMR tube. The $^1H$ NMR spectrum was recorded as soon as possible (< 1 min), and showed that complete conversion into $TsiSiMe_2Cl$ had occurred. Subsequently the compounds $(Me_3Si)_{4-n}C(SiMe_2Cl)_n$ ($n$ = 2–4) were progressively formed; thus after 10 min the composition was $(n=1)/(n=2)=30/70$. After 30 min it was $(n=1)/(n=2)/(n=3)/(n=4)=1/51/40/7$, after 24 h $(n=3)/(n=4)=63/37$, and after 168 h only the compound with $n=4$ was present. ($^1H$ NMR: $n=2$, $\delta$ 0.39 and 0.71; $n=3$, $\delta$ 0.44 and 0.78; $n=4$, $\delta$ 0.86).

(iv) A procedure identical to that described in (iii) above was carried out but with IBr in place of ICl. Conversion into $TsiSiMe_2Br$ was complete within 1 min, and progressive conversion into $(Me_3Si)_{4-n}C(SiMe_2Br)_n$ took place; after 2 h the composition was $(n=1)/(n=2)=90/10$; after 120 h, $(n=1)/(n=2)/(n=3)=25/70/5$; after 300 h, $(n=2)/(n=3)=90/10$; and after 575 h, $(n=2)/(n=3)/(n=4)=55/40/5$. ($^1H$ NMR spectra of $(Me_3Si)_{4-n}C(SiMe_2Br)_n$: $n=1$, $\delta$ 0.27 and 0.76; $n=2$, $\delta$ 0.42 and 0.89; $n=3$, $\delta$ 0.49 and 0.98; $n=4$, $\delta$ 1.05.)

(v) Hydrogen chloride was bubbled through a solution of I (0.1 mmol) in $CCl_4$ (20 $cm^3$) for 3 h at room temperature. The $^1H$ NMR spectrum showed that no reaction had occurred.

(vii) A solution of I (0.1 mmol) in $CF_3CO_2H$ (2 $cm^3$) was kept at room temperature. The $^1H$ NMR spectrum was recorded at intervals and showed progressive formation of $TsiSiMe_2OCOCF_3$ ($\delta$ 0.29 (s, 27H) and 0.63 (s, 6H)). Conversion was complete in 3 d.

*(b) Reactions of $TsiSiMe_2CH_2CH=CH_2$ (II)*

(i) A solution of II (0.12 g, 0.36 mmol) in $CCl_4$ (10 $cm^3$) containing $I_2$ (0.10 g, 0.39 mmol) was kept at room temperature and its $^1H$ NMR spectrum was recorded at intervals. Conversion into $TsiSiMe_2I$ was 18% complete in 3 h, 30% in 8 h, 55% in 23 h, 82% in 3 d, and 100% in 4 d. The solution was subsequently shaken with aqueous $NaHSO_3$ then washed, dried ($MgSO_4$), and evaporated under vacuum to leave exclusively $TsiSiMe_2I$.

(ii) The above procedure was repeated but with $Et_2O$ as solvent and at a temperature of −70°C. The $^1H$ NMR spectrum (at 35°C) showed that after 7 h ca. 7% conversion into $TsiSiMe_2I$ had occurred. (Some or all of the reaction may have taken place as the sample warmed up in the NMR tube.)

(iii) A solution of II (0.45 mmol) in $CCl_4$ (15 $cm^3$) containing $Br_2$ (0.53 mmol) was kept at room temperature. After 1 h there was 30% conversion into $TsiSiMe_2Br$ and after 5 h, 55%. After 24 h work up as in (i) above gave exclusively $TsiSiMe_2Br$.

(iv) A solution of II (0.91 mmol) and ICl (0.94 mmol) in $CCl_4$ (21 $cm^3$) was kept at room temperature. After 1 h the $^1H$ NMR spectrum showed that $TsiSiMe_2Cl$, $TsiSiMe_2I$, and II were present in 11/5/8 ratio. No further change occurred in a further 6 h.

(v) No reaction took place when HCl was bubbled through a solution of II (0.93 mmol) in $Et_2O$ (20 $cm^3$) at −70°C for 6 h and the mixture was subsequently stirred at −70°C for 10 h. A similar result was obtained when the procedure was repeated at 0°C.

(vi) No reaction occurred when HBr was bubbled for 7 h through a solution of II (1.6 mmol) in $Et_2O$ (20 $cm^3$) either at −70 or 0°C.

(vii) No reaction occurred when HI was bubbled through a solution of II (1.5 mmol) in $Et_2O$ (20 $cm^3$) at −70°C for 3 h and the mixture was subsequently allowed to warm to room temperature.

(viii) A solution of II (30 mg) in $CF_3CO_2H$ (1 $cm^3$) was kept for 0.5 h at room temperature, and the solvent was then removed under reduced pressure. The solid left was shown by its $^1H$ NMR spectrum to be $TsiSiMe_2O_2CCF_3$.

*(c) Reactions of $TsiSiMe_2C\equiv CPh$ (III)*

(i) No reaction occurred when a solution of III (0.51 mmol) and $I_2$ (0.51 mmol) in $CCl_4$ (10 $cm^3$) was kept at room temperature for 12 d or refluxed for 4 h.

(ii) A solution of III (0.83 mmol) and $Br_2$ (0.83 mmol) in $CCl_4$ (21 $cm^3$) was kept at room temperature and the $^1H$ NMR spectrum was recorded at intervals. This showed that $TsiSiMe_2Br$ was slowly formed, but the reaction was only ca. 25% complete after 7 d.

(iii) When the experiment described under (ii) above was repeated but with 3.3 mmol of $Br_2$, conversion into $TsiSiMe_2Br$ was complete within 30 min.

(iv) No reaction occurred when HCl was bubbled through a solution of III (1.3 mmol) in $Et_2O$ (30 $cm^3$) for 6 h at −70 or 0°C. A similar procedure at room temperature, however, gave complete conversion into $TsiSiMe_2Cl$.

*(d) Reactions of* $TsiSiMe_2Ph$ *(IV)*

(i) A solution of IV (0.03 mmol) in $CCl_4$ (1 $cm^3$) containing $Br_2$ (0.10 mmol) in an NMR tube was kept at 60°C. After 6 h the $^1H$ NMR spectrum indicated that about 17% conversion into $TsiSiMe_2Br$ had occurred, and after 9 d conversion was still only about 40% complete.

(ii) When the procedure described under (i) above was repeated but with $CH_3CO_2H$ as solvent, about 50% conversion into $TsiSiMe_2Br$ had occurred after 6 h and ca. 55% after 9 d.

(iii) A nitration mixture was prepared by adding 70% w/w aqueous nitric acid (5.0 g) dropwise with stirring and ice-cooling to $(CH_3CO)_2O$ (33 g) at 0°C. This was then added dropwise to a solution of IV (1 g) in $(CH_3CO)_2O$ (5 g) at 0°C. The mixture was kept at 0°C for 6 h then added to an excess of 38% aqueous $NH_3$ with ice-cooling. After extraction with ether the ethereal layer was washed, dried ($MgSO_4$), and evaporated under reduced pressure to leave an oil. This was shaken with a little EtOH and the mixture was kept at $-20$°C overnight. The solid formed was filtered off, and its $^1H$ NMR spectrum was recorded. It showed (along with a multiplet at $\delta$ 7.4–8.7) two sets of singlets, one at $\delta$ 0.35 and 0.73 in a 9/2 height ratio, and another at $\delta$ 0.40 and 0.67 ppm in a similar ratio. Attempts to separate the mixture by TLC on silica gel with various eluents were unsuccessful. Examination by GLC/MS showed that the mixture consisted of two mono-nitro isomers, $TsiSiMe_2C_4H_4NO_2$, in 3/1 ratio; the mass spectra of the two isomers were virtually identical; *m/z* 396 (40%, $[M - Me]^+$), 73 (100%).

*(e) Reactions of* $TsiSiMe_2CH_2Ph$ *(V)*

(i) A solution of V (0.30 g, 0.79 mmol) in $CH_3CO_2H$ (10 $cm^3$) containing $Br_2$ (0.81 mmol) was kept at room temperature. After 30 min the $^1H$ NMR spectrum showed that complete conversion into a single product had occurred. Removal of the solvent gave a solid, which was recrystallized from EtOH to give $TsiSiMe_2CH_2C_6H_4Br$-*p* (0.27 g, 74%), m.p. 112°C; $\delta$(H) 0.13 (s, 6H, $SiMe_2$), 0.32 (s, 27H, $SiMe_3$) and 6.8–7.4 ppm (m, 4H, with AA'BB' pattern, $C_6H_4$) (The 2H signal from the $CH_2$ group was observed but its chemical shift was not recorded.); *m/z* 443 (45%, $[M - Me]^+$), 289 (100, $[M - CH_2C_6H_4Br]^+$) (Found: C, 49.7; H, 8.3. $C_{19}H_{39}BrSi_4$ calcd.: C, 49.7; H, 8.5%).

(ii) No reaction occurred when a solution of V (0.26 mmol) in $CCl_4$ (10 $cm^3$) containing $Br_2$ (1 mmol) was kept at room temperature for 24 h.

When the procedure was repeated but with only 2 $cm^3$ of $CCl_4$, the $^1H$ NMR spectrum after 20 min was consistent with the exclusive formation of $TsiSiMe_2CH_2C_6H_4Br$-*p*. The solvent was removed to leave a solid, which was recrystallized from MeOH and then sublimed, to give $TsiSiMe_2CH_2C_6H_4Br$-*p*, with properties identical to those described under (i) above.

(iii) A nitrating mixture was prepared by adding 70% aqueous $HNO_3$ (9 g) dropwise with stirring and ice-cooling to $(CH_3CO)_2O$ (60 g) at 0°C. The solution was added dropwise with ice-cooling to a stirred solution of V (1.9 g) in $(CH_3CO)_2O$ (10 g) at 0°C. The mixture was kept at 0°C for 6 h, then worked up as described above for nitration of IV, to give a solid, which was separated into two components by TLC (silica gel; 3/1 hexane/$CH_2Cl_2$ as eluent). The first component eluted (65% of the mixture), assumed to be $TsiSiMe_2CH_2C_6H_4$ $NO_2$-*o*, had m.p. 92°C; $\delta$(H) 0.04 (s, 6H, $SiMe_2$), 0.29 (s, 27H, $SiMe_3$), 2.93 (s, 2H, $CH_2$) and 7.1–7.9 ppm (m, 4H,

$C_6H_4$); *m/z* 425 (10%, $M^+$), 410 (15, $[M - Me]^+$), 289 (40, $[M - CH_2C_6H_4NO_2]^+$), 73 (100, $[Me_3Si]^+$) (Found: C, 53.4, H, 9.4; N, 3.2. $C_{19}H_{39}NO_2Si_4$ calcd.: C, 53.6; H, 9.2; N, 3.3%). The second component (35% of mixture) had m.p. 115°C; $\delta$(H) 0.12 (s, 6H, $SiMe_2$), 0.30 (s, 27H, $SiMe_3$), 2.53 (s, 2H, $CH_2$), and 7.05–8.14 ppm (m, 4H, with AA'BB' pattern) and was judged to be $TsiSiMe_2CH_2C_6H_4NO_2$-*p* (Found: C, 53.2; H, 9.3; N, 3.1%). The mass spectrum showed the same peaks as in the first isomer, but with somewhat different relative intensities, e.g. *m/z* 425 (20%), 410 (95), 289 (85), 73 (100).

## Acknowledgements

We thank the S.E.R.C. for support, the Dow Corning Co., Ltd., for gifts of organosilicon chemicals, and Mr. R.W. Bott and Dr. P.D. Lickiss for helpful discussions. R.I.D. thanks the Libyan Government for the award of a postgraduate scholarship.

## References

1 See e.g. C. Eaborn, in H. Sakurai (Ed.), Organosilicon and Biorganosilicon Chemistry, Ellis Horwood, Chichester, 1985, pp. 123–130. J. Organomet. Chem., 239 (1982) 93.
2 C. Eaborn and S.H. Parker, J. Chem. Soc., (1955) 126.
3 E.A. Chernyshev, M.E. Dolgaya, and A.D. Petrov, Bull. Acad. Sci., U.S.S.R., (1960) 1323.
4 R.A. Benkeser and P.E. Brumfield, J. Am. Chem. Soc., 76 (1954) 904.
5 C. Eaborn, T.A. Emokpae, V.I. Sidorov, and R. Taylor, J. Chem. Soc., Perkin Trans. II, (1974) 1454.
6 R.W. Bott, C. Eaborn, and K. Leyshon, J. Chem. Soc., (1964) 1971.
7 C. Eaborn, P.B. Hitchcock, J.D. Smith, and A.C. Sullivan, J. Chem. Soc., Chem. Commun., (1983) 827.
8 P.D. Lickiss, D. Phil. Thesis, Univ. of Sussex, 1983.
9 J.L. Speier, J. Am. Chem. Soc., 75 (1953) 2930.
10 Z.H. Aiube and C. Eaborn, J. Organomet. Chem., 269 (1984) 217.
11 V.M. Vdovin, K.S. Pushchevaya and A.D. Petrov, Izvest. Akad. Nauk S.S.S.R., Ser. Khim., (1961) 1275.
12 O.N. Florensova, B. Sokolov, and L.I. Volkova, Izvest. Akad Nauk S.S.S.R., Ser. Khim, (1973) 1390.
13 C. Eaborn, J. Chem. Soc., (1952) 2846.
14 C. Eaborn, P.B. Hitchcock, and P.D. Lickiss, J. Organomet. Chem., 221 (1981) 13.
15 V.M. Vdovin, N.S. Nametkin, E.Sh. Finkel'shtein, and V.D. Oppengeim, Izvest. Akad. Nauk, S.S.S.R., Ser. Khim, (1964) 458.
16 G.A. Ayoko, personal communication.