

## SOME TETRASILYLMETHANE DERIVATIVES

COLIN EABORN\* and PAUL D. LICKISS

*School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)*

(Received May 27th, 1985)

### Summary

The preparations are described of the compounds: (i)  $C(SiMe_2X)_4$  with  $X = H, F, Cl, Br, I, OMe, OEt, OCOMe$  and  $OCOCF_3$ ; (ii)  $(HMe_2Si)_{4-n}C(SiMe_2X)_n$  with  $X = Cl, Br, I, n = 1-3$ ;  $X = OH, n = 1$  or  $2$ ; and  $X = OMe, n = 1$ ; (iii)  $(Me_3Si)_{4-n}C(SiMe_2X)_n$  with  $X = H, Cl, Br, n = 1-3$ ;  $X = I, n = 2$  or  $3$ ; and  $X = OCOMe, n = 2$ ; (iv)  $(ClSiMe_2)_3SiMe_2OH$  and  $(ClMe_2Si)_3C(SiMe_2OCOMe)$ . (Not all the products were isolated.) The reaction between  $(Me_3Si)_4C$  and IX with  $X = Cl$  or  $Br$  provide good routes to the corresponding  $C(SiMe_2X)_4$  compounds.

### Introduction

Studies of compounds in which the  $(Me_3Si)_3C$  or a related bulky ligand is present at a functional silicon centre have produced much novel chemistry [1–8]. We describe here the preparations and some reactions of compounds of the type  $(Me_3Si)_{4-n}C(SiMe_2X)_n$  and  $(HMe_2Si)_{4-n}C(SiMe_2X)_n$ , mainly from  $(Me_3Si)_4C$  or  $(HMe_2Si)_4C$ .

### Results and discussion

The compound  $(HMe_2Si)_4C$  (I) was made in two ways. The first involved the reaction between  $HMe_2SiCl, CBr_4$ , and  $Mg$  in THF (tetrahydrofuran), as described by Merker and Scott [9], which gave yields of 35–55%. The second involved reduction with  $LiAlH_4$  of  $(ClMe_2Si)_4C$ , which was itself obtained in 90% yield from the reaction of  $(Me_3Si)_4C$  with  $ICl$ . (Reaction of  $(Me_3Si)_4C$  with  $AlCl_3$ , as described by Ishikawa et al. [10], also gave  $(ClMe_2Si)_4C$  in 85% yield. Since  $HMe_2SiCl$  is relatively expensive, and since  $(Me_3Si)_4C$  can be prepared easily in good yield from  $Me_3SiCl$ , this second route to  $(HMe_2Si)_4C$  could be preferable for larger scale preparations.

Treatment of I with an excess of  $X_2$  ( $X = Cl, Br$  or  $I$ ) gave the species  $C(SiMe_2X)_4$  in good yield. The reaction of  $C(SiMe_2Br)_4$  with  $AgBF_4$  gave the tetrafluoride  $C(SiMe_2F)_4$ .

TABLE 1

$^1\text{H}$  NMR CHEMICAL SHIFTS FOR  $(\text{Me}_3\text{Si})_{4-n}\text{C}(\text{SiMe}_2\text{X})_n$ ,  $(\text{HMe}_2\text{Si})_{4-n}\text{C}(\text{SiMe}_2\text{X})_n$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) AND  $(\text{ClMe}_2\text{Si})_{4-n}\text{C}(\text{SiMe}_2\text{Br})_n$  COMPOUNDS

$(\text{Me}_3\text{Si})_{4-n}\text{C}(\text{SiMe}_2\text{X})_n$						
$n$	$\text{X} = \text{Cl}$		$\text{Br}$		$\text{I}$	
	$\text{SiMe}_3$	$\text{SiMe}_2$	$\text{Me}_3\text{Si}$	$\text{Me}_2\text{Si}$	$\text{Me}_3\text{Si}$	$\text{SiMe}_2$
1	0.29	0.61	0.27	0.76	0.36	1.08
2	0.38	0.70	0.42	0.89	0.47	1.20
3	0.44	0.78	0.49	0.98	0.60	1.35
4		0.84		1.05		1.49

  

$(\text{HMe}_2\text{Si})_{4-n}\text{C}(\text{SiMe}_2\text{X})_n$									
$n$	$\text{X} = \text{Cl}$			$\text{Br}$			$\text{I}$		
	$\text{SiMe}_2\text{Cl}$	$\text{SiMe}_2\text{H}$	$\text{SiH}$	$\text{SiMe}_2\text{Br}$	$\text{SiMe}_2\text{H}$	$\text{SiH}$	$\text{SiMe}_2\text{I}$	$\text{SiMe}_2\text{H}$	$\text{SiH}$
1	0.55	0.30	4.10	0.72	0.33	4.12	1.00	0.39	4.14 <sup>a</sup>
2	0.63	0.38	4.13	0.83	0.44	4.15	1.15	0.55	4.14 <sup>a</sup>
3	0.72	0.47	4.21	0.93	0.55	4.20	1.32	0.72	4.20
4	0.84			1.05			1.49		

  

$(\text{ClMe}_2\text{Si})_{4-n}\text{C}(\text{SiMe}_2\text{Br})_n$		
$n$	$\text{SiMe}_2\text{Cl}$	$\text{SiMe}_2\text{Br}$
1	0.84	0.99
2	0.85	0.97
3	0.84	1.04
4	0.90	1.05

<sup>a</sup> Approximate centre of overlapping multiplets.

When a solution of  $\text{Cl}_2$  in  $\text{CCl}_4$  was added dropwise to a vigorously stirred solution of I in  $\text{CCl}_4$ , monitoring by  $^1\text{H}$  NMR spectroscopy revealed the successive formation of the chlorides  $(\text{HMe}_2\text{Si})_{4-n}\text{C}(\text{SiMe}_2\text{Cl})_n$  with  $n = 1-4$ . When the spectrum indicated that roughly equal amounts of the compounds with  $n = 1-3$  were present the addition was stopped, and the products were separated by preparative GLC. A similar procedure gave the bromides  $(\text{HMe}_2\text{Si})_{4-n}\text{C}(\text{SiMe}_2\text{Br})_n$  with  $n = 1-3$ . A related procedure involving  $\text{I}_2$  likewise gave the species  $(\text{HMe}_2\text{Si})_{4-n}\text{C}(\text{SiMe}_2\text{I})_n$  with  $n = 1-3$ , as indicated by the  $^1\text{H}$  NMR spectrum of the solution, but in this case the products were not separated. Treatment of each of the compounds  $(\text{HMe}_2\text{Si})_{4-n}\text{C}(\text{SiMe}_2\text{Cl})_n$  with  $n = 1-3$  with  $\text{Br}_2$  in  $\text{CCl}_4$  gave, as expected, the corresponding mixed halide species  $(\text{BrMe}_2\text{Si})_{4-n}\text{C}(\text{SiMe}_2\text{Cl})_n$ ,  $n = 1-3$  (for relevant  $^1\text{H}$  NMR data see Table 1).

Compound I was also converted into the alkoxides  $\text{C}(\text{SiMe}_2\text{OR})_4$  ( $\text{R} = \text{Me}$  or  $\text{Et}$ ) by reaction with the appropriate alcohol ROH in the presence of  $\text{H}_2\text{PtCl}_6$  (cf. ref. 11).

The tetracarboxylates  $\text{C}(\text{SiMe}_2\text{OCOR})_4$  with  $\text{R} = \text{Me}$  or  $\text{CF}_3$  were made, respectively, by treatment of  $\text{C}(\text{SiMe}_2\text{I})_4$  with  $\text{AgO}_2\text{CMe}$  in  $\text{CH}_2\text{Cl}_2$  or  $\text{AgO}_2\text{CCF}_3$  in  $\text{CH}_2\text{Cl}_2/\text{CF}_3\text{CO}_2\text{H}$ . Interestingly, when the reaction between  $\text{C}(\text{SiMe}_2\text{Br})_4$  and  $\text{AgO}_2\text{CCF}_3$  in 1/2 molar ratio in ether was interrupted when about half of the tetrabromide had reacted, the  $^1\text{H}$  NMR spectrum of the isolated product mixture showed it to consist very predominantly of starting material,  $\text{C}(\text{SiMe}_2\text{Br})_4$ , and the

tetra-trifluoroacetate  $C(\text{SiMe}_2\text{OCOCF}_3)_4$ , with only traces of the other species. This implies that the ease of replacement of the Br substituents is markedly and progressively greater in  $(\text{BrMe}_2\text{Si})_{4-n}C(\text{SiMe}_2\text{OCOCF}_3)_n$  compounds with  $n = 1-3$  than in  $C(\text{SiMe}_2\text{Br})_4$ , and this can be attributed to anchimeric assistance by the  $\gamma\text{-OCOCF}_3$  group [6,8], since  $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{Br}$  would be effectively inert under the conditions used [7].

The bromides  $(\text{HMe}_2\text{Si})_{4-n}C(\text{SiMe}_2\text{Br})_n$  with  $n = 1, 2$  were converted into the corresponding hydroxides  $(\text{HMe}_2\text{Si})_{4-n}C(\text{SiMe}_2\text{OH})_n$  by treatment with aqueous THF, and the methoxide  $(\text{HMe}_2\text{Si})_3C(\text{SiMe}_2\text{OMe})$  was obtained by treatment of  $(\text{HMe}_2\text{Si})_3C(\text{SiMe}_2\text{Br})$  with MeOH. The lower steric hindrance resulting from the presence of hydrogen on silicon in the  $(\text{HMe}_2\text{Si})_{4-n}C(\text{SiMe}_2\text{Br})_n$  species evidently makes them much more reactive than  $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{Br}$  in this kind of reaction.

When the tetrahydroxide  $C(\text{SiMe}_2\text{OH})_4$  [4] was treated with an excess of MeCOCl (used as supplied, and so possibly containing MeCO<sub>2</sub>H and HCl), the product appeared from its <sup>1</sup>H NMR spectrum to be  $(\text{ClMe}_2\text{Si})_3\text{SiMe}_2\text{OH}$ . In contrast,  $(\text{Me}_3\text{Si})_2C(\text{SiMe}_2\text{OH})_2$  under similar conditions gave the diacetate  $(\text{Me}_3\text{Si})_2C(\text{SiMe}_2\text{OCOMe})_2$  (but later work [12] with purified MeCOCl has given  $(\text{Me}_3\text{Si})_2C(\text{SiMe}_2\text{OCOMe})(\text{SiMe}_2\text{Cl})$ ). Reaction of the tetra-acetate  $C(\text{SiMe}_2\text{OCOMe})_4$  with an excess of MeCOCl (again used as supplied) gave a single product, which appeared to be  $(\text{ClMe}_2\text{Si})_3C(\text{SiMe}_2\text{OCOMe})$ . Consideration of the various reaction modes observed must await systematic investigation of possible effects of variation in the purity of the MeCOCl used, and we note here only that it is puzzling that  $(\text{ClMe}_2\text{Si})_3\text{CSiMe}_2\text{OH}$  does not readily react further to give  $(\text{ClMe}_2\text{Si})_3\text{CSiMe}_2\text{OCOMe}$ , in view of the fact that under apparently similar conditions  $\text{TsiSiMe}_2\text{OH}$  gives  $\text{TsiSiMe}_2\text{OCOMe}$  [13].

The reaction between  $(\text{Me}_3\text{Si})_4\text{C}$  and ICl in  $\text{CCl}_4$  was monitored by <sup>1</sup>H NMR spectroscopy (cf. Table 1), and this revealed the successive formation of the species  $(\text{Me}_3\text{Si})_{4-n}C(\text{SiMe}_2\text{Cl})_n$  with  $n = 1-4$ . Preparative GLC on a mixture of the chlorides thus obtained yielded the compound  $(\text{Me}_3\text{Si})C(\text{SiMe}_2\text{Cl})_3$ . Another similar mixture of chlorides was reduced with  $\text{LiAlH}_4$ , and the corresponding hydrides  $(\text{Me}_3\text{Si})_{4-n}C(\text{SiMe}_2\text{H})_n$  with  $n = 2-4$  were separated by preparative GLC.

The reaction between  $(\text{Me}_3\text{Si})_4\text{C}$  and IBr in  $\text{CCl}_4$  was shown similarly to proceed progressively through  $(\text{Me}_3\text{Si})_{4-n}C(\text{SiMe}_2\text{Br})_n$  species with  $n = 1-3$ , finally to give a good yield of  $C(\text{SiMe}_2\text{Br})_4$ . (For the relevant <sup>1</sup>H NMR spectral data see Table 1.)

Treatment of  $(\text{Me}_3\text{Si})C(\text{SiMe}_2\text{H})_3$  with  $\text{Br}_2$  in  $\text{CCl}_4$  gave  $(\text{Me}_3\text{Si})C(\text{SiMe}_2\text{Br})_3$ , and treatment of a mixture of  $(\text{Me}_3\text{Si})_2C(\text{SiMe}_2\text{H})_2$  and  $(\text{Me}_3\text{Si})C(\text{SiMe}_2\text{H})_3$  with  $\text{I}_2$  correspondingly gave a mixture of  $(\text{Me}_3\text{Si})_2C(\text{SiMe}_2\text{I})_2$  and  $(\text{Me}_3\text{Si})C(\text{SiMe}_2\text{I})_3$ .

## Experimental

### General

(a) *Materials.* The compounds  $(\text{Me}_3\text{Si})_4\text{C}$  [7],  $(\text{Me}_3\text{Si})_2C(\text{SiMe}_2\text{OH})_2$  [5], and  $C(\text{SiMe}_2\text{OH})_4$  [4] were prepared as previously described. Solvents were dried by standard methods.

(b) *Spectra.* The <sup>1</sup>H NMR spectra were recorded (with  $\text{CCl}_4$  solutions containing  $\text{CHCl}_3$  or  $\text{CH}_2\text{Cl}_2$  as lock and reference, unless otherwise stated) at 60 MHz (Perkin-Elmer R12 spectrometer) or 90 MHz (Perkin-Elmer R32 spectrometer). The <sup>19</sup>F NMR spectra were recorded at 84.6 MHz (Perkin-Elmer R32) or 75.4 MHz (Bruker WP80); solutions were in  $\text{CCl}_4$  or  $\text{CDCl}_3$ , and chemical shifts are relative to external  $\text{CFCl}_3$ .

The IR spectra were recorded as Nujol mulls between NaCl plates on a Perkin-Elmer 157G spectrophotometer.

The mass spectra (electron impact) were recorded at 70 eV.

(c) *Procedure.* Light was excluded from all reactions involving silver salts.

*Preparation of (HMe<sub>2</sub>Si)<sub>4</sub>C*

(a) The procedure described by Merker and Scott [9], starting from CBr<sub>4</sub>, Me<sub>2</sub>SiHCl, and Mg, gave (HMe<sub>2</sub>Si)<sub>4</sub> (55%), m.p. 115°C; δ(H) 0.23 (d, 24H, SiMe<sub>2</sub>) and 4.08 (septet, 4H, SiH); ν(SiH) 2100 cm<sup>-1</sup>; *m/z* 248 (5%, [M]<sup>+</sup>), 247 (10, [M - H]<sup>+</sup>), 233 (100, [M - Me]<sup>+</sup>), 188 (15, [M - H - SiMe<sub>2</sub>H]<sup>+</sup>), 173 (35, [M - H - Me<sub>3</sub>SiH]<sup>+</sup>), 159 (25, [M - Me - Me<sub>3</sub>SiH]<sup>+</sup>), 73 (35, [Me<sub>3</sub>Si]<sup>+</sup>), 59 (10, [Me<sub>2</sub>HSi]<sup>+</sup>).

(b) A mixture of (ClMe<sub>2</sub>Si)<sub>4</sub>C (5.0 g, 0.013 mol) (prepared from (Me<sub>3</sub>Si)<sub>4</sub>C and ICl as described later) and LiAlH<sub>4</sub> (4.0 g, 0.105 mol) in THF (100 cm<sup>3</sup>) was stirred under reflux for 5 h, then cooled and treated cautiously with saturated aqueous NH<sub>4</sub>Cl (150 cm<sup>3</sup>). Extraction with light petroleum (b.p. 60–80°C; 2 × 100 cm<sup>3</sup>), followed by washing, drying (MgSO<sub>4</sub>), and evaporation of the extract left a solid, which was sublimed (90°C at atmospheric pressure) to give (HMe<sub>2</sub>Si)<sub>4</sub>C (2.4 g, 74%), with properties identical to those described above.

*Formation of compounds of the type (HMe<sub>2</sub>Si)<sub>4-n</sub>C(SiMe<sub>2</sub>X)<sub>n</sub> (n = 1–4, X = Cl, Br or I) from (HMe<sub>2</sub>Si)<sub>4</sub>C (I)*

(a) Chlorine gas was bubbled slowly into a solution of I (100 mg, 0.40 mmol) in CCl<sub>4</sub> (25 cm<sup>3</sup>) until a pale yellow-green colour persisted. The solvent was removed under vacuum to leave pure (ClMe<sub>2</sub>Si)<sub>4</sub>C (145 mg, 94%), with properties identical to those described under (c) below.

(b) A dilute solution (ca. 1 M) of Cl<sub>2</sub> in CCl<sub>4</sub> was added dropwise to a vigorously stirred solution of I (100 mg, 0.40 mmol) in CCl<sub>4</sub> (5 cm<sup>3</sup>) and the composition of the mixture was monitored by <sup>1</sup>H NMR spectroscopy. When the spectrum showed that approximately equal amounts of the three compounds (HMe<sub>2</sub>Si)<sub>4-n</sub>C(SiMe<sub>2</sub>Cl)<sub>n</sub> with *n* = 1–3 were present, the addition was stopped and the solvent was removed under vacuum. The solid left was dissolved in the minimum amount of CHCl<sub>3</sub>, and subjected to preparative GLC (2 m, 20% OV101, 180°C) to give: (i) (HMe<sub>2</sub>Si)<sub>3</sub>C(SiMe<sub>2</sub>Cl), m.p. 173°C, δ(H) 0.30 (d, 18H, SiMe<sub>2</sub>H), 0.55 (s, 6H, SiMe<sub>2</sub>Cl), and 4.10 (m, 3H, SiH); ν(SiH) 2120 cm<sup>-1</sup> (Found: C, 38.1; H, 9.3. C<sub>9</sub>H<sub>27</sub>ClSi<sub>4</sub> calcd.: C, 38.2; H, 9.6%); (ii) (HMe<sub>2</sub>Si)<sub>2</sub>C(SiMe<sub>2</sub>Cl)<sub>2</sub>, m.p. 220°C, δ(H) 0.38 (d, 12H, SiMe<sub>2</sub>H), 0.63 (s, 12H, SiMe<sub>2</sub>Cl) and 4.13 (m, 2H, SiH); ν(SiH) 2120 cm<sup>-1</sup> (Found: C, 34.0; H, 8.0. C<sub>9</sub>H<sub>26</sub>Cl<sub>2</sub>Si<sub>4</sub> calcd.: C, 34.0; H, 8.25%); (iii) (HMe<sub>2</sub>Si)C(SiMe<sub>2</sub>Cl)<sub>3</sub>, m.p. > 300°C, δ(H) 0.47 (d, 6H, SiMe<sub>2</sub>H), 0.72 (s, 18H, SiMe<sub>2</sub>Cl) and 4.21 (m, 1H, SiH), ν(SiH) 2120 cm<sup>-1</sup> (Found: C, 30.7; H, 6.9. C<sub>9</sub>H<sub>25</sub>Cl<sub>3</sub>Si<sub>4</sub> calcd.: C, 30.7; H, 6.9%).

(c) A mixture of I (100 mg, 0.40 mmol) and PCl<sub>5</sub> (350 mg, 1.70 mmol) in CCl<sub>4</sub> (25 cm<sup>3</sup>) was stirred under reflux for 5 h, after which the solvent was removed under vacuum. The residue was treated carefully with water, and the mixture was then extracted with light petroleum (b.p. 60–80°C). The extract was dried (MgSO<sub>4</sub>) and evaporated, and the solid residue was recrystallized from CCl<sub>4</sub> to give (ClMe<sub>2</sub>Si)<sub>4</sub>C (130 mg, 82%), m.p. > 300°C; δ(H) 0.85 (lit. 11, m.p. > 300°C, δ(H) 0.84); *m/z* 369 (70%, [M - Me]<sup>+</sup>), 261 (40, [M - Me - Me<sub>3</sub>SiCl]<sup>+</sup>), 241 (15, [M - Me<sub>3</sub>SiCl - Cl]<sup>+</sup>), 73 (35) 59 (15) (the isotope pattern was as expected, so that the base peak (100%) was at *m/z* 371).

(d) A 1 M solution of ICl (10 mmol) in  $\text{CCl}_4$  (10  $\text{cm}^3$ ) was added with stirring to a solution of I (100 mg, 0.40 mmol) in  $\text{CCl}_4$  (25  $\text{cm}^3$ ). The mixture was kept at room temperature for 30 min then shaken with saturated aqueous  $\text{NaHSO}_3$  (2  $\times$  25  $\text{cm}^3$ ). The organic layer was separated, dried ( $\text{MgSO}_4$ ), and evaporated, to leave exclusively  $(\text{ClMe}_2\text{Si})_4\text{C}$  (140 mg, 90%), with properties identical to those described in (c) above.

(e) A 1 M solution of  $\text{Br}_2$  in  $\text{CCl}_4$  was added dropwise with stirring to a solution of I (100 mg, 0.40 mmol) in  $\text{CCl}_4$  (10  $\text{cm}^3$ ) until the colour persisted (ca. 2  $\text{cm}^3$  was needed). The solvent was then removed under vacuum, and the residual solid was sublimed (150°C at 0.05 mmHg) to give  $(\text{BrMe}_2\text{Si})_4\text{C}$  (0.21 g, 93%), m.p. > 300°C;  $\delta(\text{H})$  1.05 (s,  $\text{SiMe}_2\text{Br}$ );  $m/z$  545 ( $[\text{M} - \text{Me}]^+$ ), 481 (base peak set,  $[\text{M} - \text{Br}]^+$ ), 393 ( $[\text{M} - \text{Me}_3\text{SiBr} - \text{Me}]^+$ ), 329 ( $[\text{M} - \text{Me}_3\text{SiBr} - \text{Br}]^+$ ), 137 ( $[\text{BrMe}_2\text{Si}]^+$ ), 73, 59 (all peaks with expected isotope patterns) (Found: C, 19.5; H, 4.3.  $\text{C}_9\text{H}_{24}\text{Br}_4\text{Si}_4$  calcd.: C, 19.2; H, 4.3%).

(f) A 1 M solution of  $\text{Br}_2$  in  $\text{CCl}_4$  was added dropwise to a vigorously stirred solution of I (100 mg, 0.40 mmol) in  $\text{CCl}_4$  (5  $\text{cm}^3$ ) and the composition of the solution was monitored by  $^1\text{H}$  NMR spectroscopy. When the spectrum revealed that approximately equal amounts of the three compounds  $(\text{HMe}_2\text{Si})_{4-n}\text{C}(\text{SiMe}_2\text{Br})_n$  with  $n = 1-3$  were present the addition was stopped, and the solvent was removed under vacuum. The residual solid was taken up in the minimum of  $\text{CHCl}_3$ , and subjected to preparative GLC (2 m, 20% OV101, 220°C) to give (as white solids): (i)  $(\text{HMe}_2\text{Si})_3\text{CSiMe}_2\text{Br}$ ;  $\delta(\text{H})$  0.33 (d, 18H,  $\text{SiMe}_2\text{H}$ ), 0.72 (s, 6H,  $\text{SiMe}_2\text{Br}$ ), and 4.12 (m, 3H, SiH);  $\nu(\text{SiH})$  2120  $\text{cm}^{-1}$  (Found: C, 33.4, H, 8.0.  $\text{C}_9\text{H}_{27}\text{BrSi}_4$  calcd.: C, 33.0, H, 8.3%). (ii)  $(\text{HMe}_2\text{Si})_2\text{C}(\text{SiMe}_2\text{Br})_2$ ,  $\delta(\text{H})$  0.44 (d, 12H,  $\text{SiMe}_2\text{H}$ ), 0.83 (s, 12H,  $\text{SiMe}_2\text{Br}$ ), and 4.15 (m, 2H, SiH),  $\nu(\text{SiH})$  2120  $\text{cm}^{-1}$  (Found: C, 26.8; H, 6.1.  $\text{C}_9\text{H}_{26}\text{Br}_2\text{Si}_4$  calcd.: C, 26.6; H, 6.45%); (iii)  $(\text{HMe}_2\text{Si})\text{C}(\text{SiMe}_2\text{Br})_3$ ,  $\delta(\text{H})$  0.55 (d, 6H,  $\text{SiMe}_2\text{H}$ ), 0.93 (s, 18H,  $\text{SiMe}_2\text{Br}$ ), and 4.20 (m, 1H, SiH);  $\nu(\text{SiH})$  2120  $\text{cm}^{-1}$ . (Found: C, 22.5; H, 5.3.  $\text{C}_9\text{H}_{25}\text{Br}_3\text{Si}_4$  calcd.: C, 22.7; H, 5.2%).

(g) To a solution of  $(\text{HMe}_2\text{Si})_4\text{C}$  (500 mg, 2.0 mmol) in  $\text{CCl}_4$  (10  $\text{cm}^3$ ), iodine was added until some remained undissolved on stirring. The mixture was stirred at room temperature for 24 h then the solution was decanted from the remaining solid iodine and shaken with saturated aqueous sodium thiosulphate (2  $\times$  25  $\text{cm}^3$ ). The organic layer was separated, dried and evaporated, and the solvent was removed under vacuum to leave a solid, which was recrystallized from acetone to give  $(\text{IME}_2\text{Si})_4\text{C}$  (1.15 g, 75%), m.p. > 320°C;  $\delta(\text{H})$  1.49 (br s);  $m/z$  624 (100%,  $[\text{M} - \text{HI}]^+$ ), 536 (10,  $[\text{M} - \text{Me}_3\text{SiI} - \text{MeH}]^+$ ), 424 (90,  $[\text{M} - \text{Me}_3\text{SiI} - \text{HI}]^+$ ), 313 (30), 185 (30,  $[\text{IME}_2\text{Si}]^+$ ).

(h) The procedure described under (g) was repeated but without the excess of solid iodine, and the reaction was monitored by  $^1\text{H}$  NMR spectroscopy. After 2.5 h, in addition to the peaks from I there was also a set of peaks at  $\delta$  0.39 (d, 18H,  $\text{SiMe}_2\text{H}$ ) and 1.00 (s, 6H,  $\text{SiMe}_2\text{I}$ ), attributable to  $(\text{HMe}_2\text{Si})_3\text{SiMe}_2\text{I}$  and another at  $\delta$  0.55 (d, 12H,  $\text{SiMe}_2\text{H}$ ) and 1.15 (s, 12H,  $\text{SiMe}_2\text{I}$ ) attributable to  $(\text{HMe}_2\text{Si})_2\text{C}(\text{SiMe}_2\text{I})_2$  (there was also a multiplet centred at  $\delta$  4.14 attributable to SiH resonances); the species  $(\text{HMe}_2\text{Si})_{4-n}\text{C}(\text{SiMe}_2\text{I})_n$  with  $n = 0, 1$ , and 2, respectively, were present in ca. 45/40/15 ratio. After 42 h the peaks for the compounds with  $n = 0-2$  were absent, but there was a set of peaks at  $\delta$  0.72 (d, 6H,  $\text{SiMe}_2\text{H}$ ), 1.32 (s, 18H,  $\text{SiMe}_2\text{I}$ ) and 4.20 (m, 1H, SiH) attributable to  $(\text{HMe}_2\text{Si})\text{C}(\text{SiMe}_2\text{I})_3$ , and a broad singlet at  $\delta$  1.49 attributable to  $\text{C}(\text{SiMe}_2\text{I})_4$ ; these two compounds were present in ca. 1/3 ratio.

*Formation of the compounds  $(HMe_2Si)_{4-n}C(SiMe_2OH)_n$ ,  $n = 1$  or  $2$*

(a) Some  $(HMe_2Si)_3CSiMe_2Br$  (ca. 10 mg) was dissolved in THF (2 cm<sup>3</sup>) containing 5 vol.% of H<sub>2</sub>O. The solution was stirred for 2 h then evaporated under vacuum. The solid left had a <sup>1</sup>H NMR spectrum consistent with exclusive formation of  $(HMe_2Si)_3C(SiMe_2OH)$ ;  $\delta(H)$  0.29 (s, 6H, SiMe<sub>2</sub>OH), 0.32 (d, 18H, SiMe<sub>2</sub>H), 1.43 (br s, 1H, OH), and 4.12 (m, 3H, SiH).

(b) A similar procedure starting from  $(HMe_2Si)_2C(SiMe_2Br)_2$  gave exclusively  $(HMe_2Si)_2C(SiMe_2OH)_2$ ;  $\delta(H)$  0.29 (s, 12H, SiMe<sub>2</sub>OH), 0.30 (d, 12H, SiMe<sub>2</sub>H), 3.56 (br s, 2H, OH), and 4.13 (m, 2H, SiH).

*Reaction of  $(HMe_2Si)_3C(SiMe_2Br)$  with MeOH*

A solution of  $(HMe_2Si)_3C(SiMe_2Br)$  (ca. 10 mg) in MeOH (2 cm<sup>3</sup>) was stirred at room temperature for 2 h then evaporated under reduced pressure. The <sup>1</sup>H NMR spectrum of the product was consistent with the greatly predominant formation of  $(HMe_2Si)_3C(SiMe_2OMe)$   $\delta(H)$  0.25 and 0.29 (together equivalent to 24H, presumably because of overlapping of the SiMe<sub>2</sub>H doublet with the SiMe<sub>2</sub>OMe singlet), 3.42 (s, 3H, OMe), and 4.09 (m, 3H, SiH) but there was a small additional peak at  $\delta$  0.34.

*Formation of compounds of the type  $(Me_3Si)_{4-n}C(SiMe_2X)_n$  ( $n = 1-4$ ,  $X = Cl, Br, I$ ) from  $(Me_3Si)_4C$  (II)*

(a) A mixture of II (1.0 g, 3.3 mmol) with a 5 M solution of ICl in CCl<sub>4</sub> (15 cm<sup>3</sup>, 75 mmol) was stirred at room temperature for 2 h then shaken with saturated aqueous sodium thiosulphate (2 × 25 cm<sup>3</sup>). The organic layer was separated, washed, dried (MgSO<sub>4</sub>), and evaporated, to leave a solid, which was recrystallized from CCl<sub>4</sub> to give  $C(SiMe_2Cl)_4$  (1.10 g, 86%), with properties identical to those described above.

(b) The reaction between II, AlCl<sub>3</sub> and Me<sub>3</sub>SiCl, as described by Ishikawa et al. [10], was also used to make  $C(SiMe_2Cl)_4$ , in 85% yield.

(c) A reaction between II and ICl was carried out as described in (a) above but with monitoring by <sup>1</sup>H NMR spectroscopy. When the spectrum indicated that  $Me_3SiC(SiMe_2Cl)_3$  formed about 50% of the products the mixture was worked up as before, but the initial solid obtained was taken up in a little CH<sub>2</sub>Cl<sub>2</sub> and the solution was subjected to preparative GLC (2 m, 5% SE52, 200°C), which gave (as solids) (i) a little  $C(SiMe_2Cl)_4$ , (ii)  $(Me_3Si)_2C(SiMe_2Cl)_2$ ,  $\delta(H)$  0.29 (s, 18H, SiMe<sub>3</sub>) and 0.61 (s, 12H, SiMe<sub>2</sub>Cl), and (iii)  $(Me_3Si)C(SiMe_2Cl)_3$ , m.p. > 320°C,  $\delta(H)$  0.44 (s, 9H, SiMe<sub>3</sub>) and 0.78 (s, 18H, SiMe<sub>2</sub>),  $m/z$  349 (90%,  $[M - Me]^+$ ), 256 (15,  $[M - Me_3SiCl]^+$ ), 241 (90,  $[M - Me_3SiCl - Me]^+$ ), 221 (20,  $[M - Me_3SiCl - Cl]^+$ ), 93 (30,  $[Cl_2MeSi]^+$ , 73 (80), 59 (30,  $[HMe_2Si]^+$ ) (the isotope patterns were as expected, so that the base peak was at 351) Found: C, 33.0; H, 7.4. C<sub>10</sub>H<sub>27</sub>Cl<sub>3</sub>Si<sub>4</sub> calcd.: C, 32.8; H, 7.4%.

(d) The procedure described in the preceding experiment, (c), was repeated, but the crude solid product was stirred under reflux for 3 h with LiAlH<sub>4</sub> (1.0 g, 26 mmol) in THF (25 cm<sup>3</sup>). The mixture was then very cautiously added to the ice-cold saturated aqueous NH<sub>4</sub>Cl (50 cm<sup>3</sup>), and the organosilicon products were extracted with light petroleum (b.p. 60–80°C). The organic layer was washed, dried (MgSO<sub>4</sub>) and evaporated, and the residual solid was taken up in the minimum amount of acetone. Preparative GLC (2 m, 5% SE52, 180°C) then gave (i)  $(Me_3Si)_2C(SiMe_2H)_2$ ,  $\delta(H)$  0.16 (s, 18H, SiMe<sub>3</sub>), 0.24 (d, 12H, SiMe<sub>2</sub>), and 4.11 (m, 2H, SiH) (values identical to those from an authentic sample [14]); (ii) a little  $C(SiMe_2H)_4$ ; and (iii)

$(\text{Me}_3\text{Si})\text{C}(\text{SiMe}_2\text{H})_3$ , m.p. 155–157°C;  $\delta(\text{H})$  0.17 (s, 9H,  $\text{SiMe}_3$ ), 0.25 (d, 18H,  $\text{SiMe}_2$ ), and 4.11 (m, 3H, SiH);  $\nu(\text{SiH})$  2100  $\text{cm}^{-1}$ .

(e) The procedure described under (d) was repeated up to the isolation of the product mixture from the reduction. This mixture was then dissolved in  $\text{CCl}_4$  and an excess of  $\text{I}_2$  was added. The solution was stirred for 18 h at room temperature, after which the  $^1\text{H}$  NMR spectrum showed a set of resonances, at  $\delta$  0.47 and 1.20 in 3/2 ratio, attributable to  $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{I})_2$ , and another set at  $\delta$  0.60 and 1.35, in 1/2 ratio, attributable to  $(\text{Me}_3\text{Si})\text{C}(\text{SiMe}_2\text{I})_3$ .

(f) The procedure described under (a), above, was repeated but with IBr in place of ICl, and with stirring for 18 h. The crude product was sublimed to give  $\text{C}(\text{SiMe}_2\text{Br})_4$  (85%), with properties identical to those described earlier.

Monitoring by  $^1\text{H}$  NMR spectroscopy showed that the reduction proceeded stepwise through  $(\text{Me}_3\text{Si})_3\text{C}(\text{SiMe}_2\text{Br})$ ,  $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Br})_2$ , and  $(\text{Me}_3\text{Si})\text{C}(\text{SiMe}_2\text{Br})_3$ .

(g) A 1 M solution of  $\text{Br}_2$  in  $\text{CCl}_4$  was added dropwise to a stirred solution of  $(\text{Me}_3\text{Si})\text{C}(\text{SiMe}_2\text{H})_3$  (50 mg, 0.19 mmol) in  $\text{CCl}_4$  (5  $\text{cm}^3$ ) until the colour persisted. The solvent was removed under vacuum and the residual solid was sublimed (130°C at 0.1 mmHg) to give  $(\text{Me}_3\text{Si})\text{C}(\text{SiMe}_2\text{Br})_3$  (85 mg, 89%), m.p. > 300°C (sealed tube);  $\delta(\text{H})$  0.49 (s, 9H,  $\text{SiMe}_3$ ) and 0.98 (s, 18H,  $\text{SiMe}_2$ );  $m/z$  481 (30%,  $[\text{M} - \text{Me}]^+$ ), 417 (15,  $[\text{M} - \text{Br}]^+$ ); 344 (15,  $[\text{M} - \text{Me}_3\text{SiBr}]^+$ ), 329 (40,  $[\text{M} - \text{Me}_3\text{SiBr} - \text{Me}]^+$ ); 265 (30,  $[\text{M} - \text{Me}_3\text{SiBr} - \text{Br}]^+$ ), 139 (30,  $[\text{Me}_2\text{BrSi}]^+$ ); 113, (20), 83 (25), 59 (50) (the isotope patterns were as expected, so that, e.g., the peaks at  $m/z$  483 and 485 had intensities of 85%) (Found: C, 25.0; H, 5.1.  $\text{C}_{10}\text{H}_{27}\text{Br}_3\text{Si}_4$  calcd.: C, 24.05; H, 5.45%).

*Preparations of the compounds  $(\text{ClMe}_2\text{Si})_{4-n}\text{C}(\text{SiMe}_2\text{Br})_n$  ( $n = 1-3$ )*

(a) A 1 M solution of  $\text{Br}_2$  in  $\text{CCl}_4$  was added dropwise to a stirred solution of  $(\text{HMe}_2\text{Si})\text{C}(\text{SiMe}_2\text{Cl})_3$  (ca. 10 mg) in  $\text{CCl}_4$  (1  $\text{cm}^3$ ) until the colour persisted. The solvent was then removed under vacuum, and the residue was sublimed to give  $(\text{ClMe}_2\text{Si})_3\text{C}(\text{SiMe}_2\text{Br})$ , m.p. > 300°C;  $\delta(\text{H})$  0.85 (s, 18H,  $\text{SiMe}_2\text{Cl}$ ) and 0.99 (s, 6H,  $\text{SiMe}_2\text{Br}$ );  $m/z$  413 (50%,  $[\text{M} - \text{Me}]^+$ ), 349 (25,  $[\text{M} - \text{Br}]^+$ ), 305 (30,  $[\text{M} - \text{Me}_3\text{SiCl} - \text{Me}]^+$ ), 261 (20,  $[\text{M} - \text{Me}_3\text{SiBr} - \text{Me}]^+$ ), 241 (30,  $[\text{M} - \text{Me}_3\text{SiBr} - \text{Cl}]^+$ ); 93 (10,  $[\text{Me}_2\text{ClSi}]^+$ ), 73 (65), 59 (30) (the isotope patterns were as expected, so that the base peak was at  $m/z$  415) (Found: C, 25.5; H, 5.5.  $\text{C}_9\text{H}_{24}\text{BrCl}_3\text{Si}_4$  calcd.: C, 25.1; H, 5.6%).

(b) A similar procedure to that described under (a) but starting from  $(\text{HMe}_2\text{Si})_2\text{C}(\text{SiMe}_2\text{Cl})_2$ , gave  $(\text{ClMe}_2\text{Si})_2\text{C}(\text{SiMe}_2\text{Br})_2$ , m.p. > 300°C;  $\delta(\text{H})$  0.84 (s, 12H,  $\text{SiMe}_2\text{Cl}$ ) and 0.97 (s, 12H,  $\text{SiMe}_2\text{Br}$ );  $m/z$  457 (40,  $[\text{M} - \text{Me}]^+$ ), 393 (45,  $[\text{M} - \text{Br}]^+$ ), 349 (35,  $[\text{M} - \text{Me}_3\text{SiCl} - \text{Me}]^+$ ), 285 (40,  $[\text{M} - \text{Me}_3\text{SiBr} - \text{Cl}]^+$ ), 241 (30,  $[\text{M} - \text{Me}_3\text{SiBr} - \text{Br}]^+$ ); 135 (35,  $[\text{Me}_2\text{BrSi}]^+$ ), 127 (25), 113 (25,  $[\text{Cl}_2\text{MeSi}]^+$ ), 93 (75,  $[\text{ClMe}_2\text{Si}]^+$ ), 83 (40), 73 (95), 59 (45) (the isotope pattern was as expected, so that the base peak was at  $m/z$  459) (Found: C, 23.0; H, 5.1.  $\text{C}_9\text{H}_{24}\text{Br}_2\text{Cl}_2\text{Si}_4$  calcd.: C, 22.7; H, 5.1%).

(c) A similar procedure to that described under (a), but starting from  $(\text{HMe}_2\text{Si})_3\text{C}(\text{SiMe}_2\text{Cl})$ , gave  $(\text{ClMe}_2\text{Si})\text{C}(\text{SiMe}_2\text{Br})_3$ , m.p. > 300°C;  $\delta(\text{H})$  0.90 (s, 6H,  $\text{SiMe}_2\text{Cl}$ ) and 1.04 (s, 18H,  $\text{SiMe}_2\text{Br}$ );  $m/z$  501 (25%,  $[\text{M} - \text{Me}]^+$ ), 437 (45,  $[\text{M} - \text{Br}]^+$ ), 392 (10,  $[\text{M} - \text{Me}_3\text{SiCl} - \text{MeH}]^+$ ), 349 (30,  $[\text{M} - \text{Me}_3\text{SiBr} - \text{Me}]^+$ ), 329 (15,  $[\text{M} - \text{Me}_3\text{SiCl} - \text{Br}]^+$ ), 285(35,  $[\text{M} - \text{Me}_3\text{SiBr} - \text{Br}]^+$ ), 137 (45), 127 (25),

113 (25), 93 (40), 83 (40), 73 (100), 59 (70) (the isotope patterns were as expected) (Found: C, 20.9; H, 4.7.  $C_9H_{24}Br_3ClSi_4$  calcd.: C, 20.8, H, 4.65%).

*Preparation of the compounds  $C(SiMe_2X)_4$  with  $X = F, OMe, OEt, OCOMe, or OCOCF_3$*

(a) A solution of  $C(SiMe_2Br)_4$  (0.50 g, 0.89 mmol) in  $CH_2Cl_2$  (25 cm<sup>3</sup>) was stirred with  $AgBF_4$  (0.78 g, 4.0 mmol) under  $N_2$  for 3 h. The solution was filtered and then evaporated. The solid residue was sublimed to give a solid which was identified from its NMR spectra as  $C(SiMe_2F)_4$  (0.20 g, 70%);  $\delta(H)$  0.47 (d,  $J$  7 Hz);  $\delta(F)$  -145.5 ppm (m,  $J$  7 Hz).

(b) Use of Merker and Scott's method [11], starting from  $(HMe_2Si)_4C$ ,  $H_2PtCl_6$ , and MeOH or EtOH gave: (i)  $C(SiMe_2OMe)_4$  (70%),  $\delta(H)$  0.22 (s, 24H,  $SiMe_2$ ) and 3.33 (s, 12H, OMe),  $m/z$  368 (1%,  $[M]^+$ ), 353 (40,  $[M - Me]^+$ ); 249 (10,  $[M - Me_3SiOMe - Me]^+$ ); 233 (100,  $[M - Me_3SiOMe - OMe]^+$ , 217 (60), 169 (10), 89 (10), 73 (10), 59 (10); (ii)  $C(SiMe_2OEt)_4$  (50%),  $\delta(H)$  0.29 (s, 24H,  $SiMe_2$ ), 1.17 (t, 12H,  $CH_2CH_3$ ) and 3.65 (q, 8H,  $CH_2CH_3$ ).

(c) (i) A solution of  $C(SiMe_2I)_4$  (0.50 g, 0.65 mmol) in  $CH_2Cl_2$  (25 cm<sup>3</sup>) was stirred vigorously with  $AgOCOMe$  (0.50 g, 3.0 mmol) at room temperature for 2 h then filtered, and the solvent was removed under reduced pressure. The residue was sublimed (120°C at 0.2 mmHg) to give a solid, which from its spectra was judged to be exclusively  $C(SiMe_2OCOMe)_4$  (0.25 g, 80%),  $\delta(H)$  0.57 (s, 24H,  $SiMe_2$ ) and 1.99 (s, 12H, OMe),  $\nu(C=O)$  1730 cm<sup>-1</sup>.

(ii) The reaction was repeated but with a deficiency of  $AgOCOMe$  (1.3 mmol, compared with 0.65 mmol of  $C(SiMe_2I)_4$ ). After 15 min stirring the <sup>1</sup>H NMR spectrum showed that only  $C(SiMe_2I)_4$  and  $C(SiMe_2OCOMe)_4$  were present.

(d) (i) Silver carbonate (0.41 g, 1.50 mmol) was dissolved in  $CF_3CO_2H$  (25 cm<sup>3</sup>) and  $C(SiMe_2I)_4$  (0.50 g, 0.65 mmol) was added. Sufficient  $CH_2Cl_2$  (ca. 10 cm<sup>3</sup>) was added to bring all the  $C(SiMe_2I)_4$  into solution, and the solution was stirred at room temperature for 2 h. The solution was then filtered, and evaporated under vacuum to leave a solid (0.40 g, 57%), the spectra of which indicated that it was exclusively  $C(SiMe_2OCOCF_3)_4$ ;  $\delta(H)$  0.78,  $\delta(F)$  -76.2 ppm,  $\nu(C=O)$  1765 cm<sup>-1</sup>.

(ii) A solution of  $C(SiMe_2Br)_4$  (0.25 g, 0.44 mmol) in  $Et_2O$  (10 cm<sup>3</sup>) was stirred with  $AgO_2CCF_3$  (0.19 g, 0.88 mmol) for 2 h. The solution was then filtered and evaporated under vacuum to leave a solid. This was taken up in  $CCl_4$ , and the <sup>1</sup>H NMR spectrum recorded. This showed, along with several very small peaks between  $\delta$  0.1 and 0.5, two singlets of equal height, at  $\delta$  0.78 and 1.05, which can be assigned to  $C(SiMe_2OCOCF_3)_4$  and  $C(SiMe_2Br)_4$  respectively.

*Reaction of  $C(SiMe_2OH)_4$  with  $CH_3COCl$ . Formation of  $(CMe_2Si)_3C(SiMe_2OH)$*

(a) A solution of  $C(SiMe_2OH)_4$  (100 mg, 0.30 mmol) in  $MeCOCl$  (5 cm<sup>3</sup>) was stirred at room temperature under dry  $N_2$  for 20 min. The volatile material was then removed under vacuum to leave a solid, the <sup>1</sup>H NMR spectrum of which showed two sharp singlets at  $\delta$  0.52 and 0.77 (attributable to  $SiMe_2OH$  and  $SiMe_2Cl$ , respectively) in 1/3 ratio, and a small broad peak at  $\delta$  1.34 (attributable to OH). These data indicate that the product was exclusively  $(CMe_2Si)_3C(SiMe_2OH)$ .

(b) When the reaction was repeated, but with a 1/1 mixture of  $MeCOCl$  and  $Me_2CO$  as solvent, and with removal of solvent under vacuum after only 5 min stirring, the solid obtained gave an <sup>1</sup>H NMR spectrum showing six singlets and a



small broad peak at  $\delta$  1.34 which could be assigned to  $(\text{ClMe}_2\text{Si})\text{C}(\text{SiMe}_2\text{OH})_3$  ( $\delta$  0.40 and 0.65 in 1/3 ratio),  $(\text{ClMe}_2\text{Si})_2\text{C}(\text{SiMe}_2\text{OH})_2$  ( $\delta$  0.46 and 0.72 in 1/1 ratio), and  $(\text{ClMe}_2\text{Si})_3\text{C}(\text{SiMe}_2\text{OH})$  ( $\delta$  0.52, 0.77, and 1.34). These three products were in ca. 2/2/1 ratio.

#### *Hydrolysis of $(\text{ClMe}_2\text{Si})_3\text{SiMe}_2\text{OH}$*

Some  $(\text{ClMe}_2\text{Si})_3\text{C}(\text{SiMe}_2\text{OH})$  (ca. 10 mg) was dissolved in THF (2 cm<sup>3</sup>) containing 5 vol.% H<sub>2</sub>O. The solution was set aside for 18 h then evaporated under vacuum, to leave a white solid which was insoluble in CCl<sub>4</sub>. Its <sup>1</sup>H NMR spectrum in (CD<sub>3</sub>)<sub>2</sub>CO was identical to that reported for C(SiMe<sub>2</sub>OH)<sub>4</sub> [4].

#### *Formation of $(\text{ClMe}_2\text{Si})_3\text{C}(\text{SiMe}_2\text{OCOMe})$ . Reaction of $\text{C}(\text{SiMe}_2\text{OCOMe})_4$ with MeCOCl*

A solution of C(SiMe<sub>2</sub>OCOMe)<sub>4</sub> (50 mg, 0.10 mmol) in MeCOCl (5 cm<sup>3</sup>) was stirred at room temperature for 18 h under N<sub>2</sub>. Volatile materials were removed under vacuum to leave a solid, the <sup>1</sup>H NMR spectrum of which was consistent with the exclusive formation of  $(\text{ClMe}_2\text{Si})_3\text{C}(\text{SiMe}_2\text{OCOMe})$ ;  $\delta(\text{H})$  0.72 (s, 18H, SiMe<sub>2</sub>Cl), 0.76 (s, 6H, SiMe<sub>2</sub>OCOMe), and 2.04 (s, 3H, COMe);  $\nu(\text{C}=\text{O})$  1730 cm<sup>-1</sup>.

#### *Reaction of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OH})_2$ with MeCOCl. Formation of $(\text{Me}_3\text{Si})_2\text{C}(\text{Si}_2\text{OCOMe})_2$*

A solution of  $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OH})_2$  (100 mg, 0.32 mmol) in MeCOCl (5 cm<sup>3</sup>) was stirred at room temperature for 30 min then evaporated under vacuum. The residue was sublimed under vacuum to give  $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OCOMe})_2$  (117 mg, 93%) with spectra identical to those of an authentic sample [8];  $\delta(\text{H})$  0.28 (s, 18H, SiMe<sub>3</sub>), 0.55 (s, 12H, SiMe<sub>2</sub>), and 2.02 (s, 6H, CMe);  $\nu(\text{C}=\text{O})$  1750 cm<sup>-1</sup>.

#### **Acknowledgements**

We thank the S.E.R.C. for support, Mr. A.M. Greenway for the mass spectra, and Dow Corning Ltd., for gifts of organosilicon chemicals.

#### **References**

- 1 C. Eaborn in H. Sakurai (Ed.), *Organosilicon and Biorganosilicon Chemistry*, Ellis Horwood, Chichester, 1985, pp. 123–130.
- 2 C. Eaborn, *J. Organomet. Chem.*, 239 (1982) 93.
- 3 C. Eaborn and A. Saxena, *J. Chem. Soc., Chem. Commun.*, (1984) 1482; *J. Organomet. Chem.*, 271 (1984) 33.
- 4 C. Eaborn, P.B. Hitchcock, and P.D. Lickiss, *J. Organomet. Chem.*, 264 (1984) 119.
- 5 C. Eaborn, P.D. Lickiss, and N.A. Ramadan, *J. Chem. Soc., Perkin Trans. II*, (1984) 267.
- 6 C. Eaborn and D.E. Reed, *J. Chem. Soc., Chem. Commun.*, (1983) 495.
- 7 C. Eaborn, D.A.R. Happer, S.P. Hopper, and K.D. Safa, *J. Organomet. Chem.*, 188 (1980) 179.
- 8 C. Eaborn and S.P. Hopper, *J. Organomet. Chem.*, 170 (1979) C51.
- 9 R.L. Merker and M.J. Scott, *J. Org. Chem.*, 29 (1964) 953.
- 10 M. Ishikawa, M. Kumada, and H. Sakurai, *J. Organomet. Chem.*, 23 (1970) 63.
- 11 R.L. Merker and M.J. Scott, *J. Org. Chem.*, 28 (1963) 2717.
- 12 A.D. Taylor, personal communication.
- 13 C. Eaborn and K.D. Safa, *J. Organomet. Chem.*, 234 (1982) 7; R.I. Damja and C. Eaborn, *ibid.*, 290 (1985) 267.
- 14 C. Eaborn and D.E. Reed, *J. Chem. Soc., Perkin Trans II*, (1985) in press.