

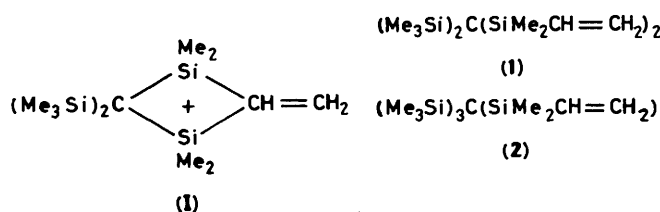
Reactions of Bis[dimethyl(vinyl)silyl]bis(trimethylsilyl)methane, $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)_2$

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The compound $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)_2$ (1) reacts in CCl_4 with halogens X_2 where $\text{X} = \text{Cl}, \text{Br},$ or I , to give the corresponding $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{X})_2$ species, and with ICl to give $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Cl})_2$; the reaction with Br_2 apparently initially gives addition products, which decompose on work-up. Reaction with AlCl_3 in CCl_4 gives $(\text{Me}_3\text{Si})_n\text{C}(\text{SiMe}_2\text{Cl})_{4-n}$ ($n = 0-2$) species. The reaction with $\text{CF}_3\text{CO}_2\text{H}$ at 60°C gives initially $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)(\text{SiMe}_2\text{O}_2\text{CCF}_3)$, which subsequently reacts *ca.* 20 times as slowly to give $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{O}_2\text{CCF}_3)_2$. There is no indication that the proximity of one vinyl group affects the reactivity at the other in these reactions of (1).

We recently showed that the vinyl group in compounds of the type $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)(\text{SiMe}_2\text{X})$ can provide substantial anchimeric assistance to the loss of X^- , *e.g.* in the reactions with MeOH or with Ag^+ salts, which are thought to proceed *via* the vinyl-bridged cations (I).^{1,2} We thus thought it of interest to examine the reactions of the divinyl compound (1) with electrophiles in order to see whether one vinyl group would have any significant influence on reaction at the other. In some cases direct comparison was made with reactions of the mono-vinyl compound (2).



Results and Discussion

Compound (1) was obtained by crossmetallation of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)\text{Cl}$ with BuLi in THF -hexane ($\text{THF} =$ tetrahydrofuran) at -100°C to give $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)\text{Li}$, and treatment of the latter with $\text{Me}_2(\text{CH}_2=\text{CH})\text{SiCl}$. The $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)\text{Cl}$ was itself made, as previously described,² by crossmetallation of $(\text{Me}_3\text{Si})_2\text{CCl}_2$ at -110°C with one equivalent of BuLi (added in hexane solution precooled to -80°C) followed by treatment with $\text{Me}_2(\text{CH}_2=\text{CH})\text{SiCl}$, but on one occasion, when the BuLi solution was not cooled before addition, and the metallation was carried out at -100°C , the product was (1), formed in 66% yield based on the amount of $\text{Me}_2(\text{CH}_2=\text{CH})\text{SiCl}$ taken. Allowing the temperature to rise to -100°C may have played a part, but it is possible that too rapid addition of the BuLi solution without precooling and perhaps with inadequate stirring allowed a local concentration of the BuLi to develop so that the initially formed $(\text{Me}_3\text{Si})_2\text{C}(\text{Cl})\text{Li}$ was converted into $(\text{Me}_3\text{Si})_2\text{ClLi}_2$ before the reagents were dispersed. It is noteworthy that $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{H})_2$ has frequently been obtained in quite high yields after treatment of $(\text{Me}_3\text{Si})_2\text{CCl}_2$ with BuLi followed by addition of Me_2SiHCl .³

Reactions with Halogens, Hydrogen Halides, and AlCl_3 .—Compound (1) (0.10 mmol) did not react detectably with a two molar proportion of I_2 (0.20 mmol) in CCl_4 (20 cm^3) during 7 days at room temperature followed by 6 h under reflux. When a large excess of I_2 (1.0 mmol) was used under otherwise similar conditions, after 18 h under reflux the ^1H n.m.r. spectrum showed (1), $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)(\text{SiMe}_2\text{I})$,

and $(\text{Me}_3\text{Si})_2(\text{SiMe}_2\text{I})_2$ to be present in *ca.* 55:25:20 ratio, and after 5 days only $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{I})_2$ was present. There was no indication of the intermediacy of products of addition of I_2 to the double bond.

When (1) was treated for 2 h with an excess of Br_2 in CCl_4 under reflux the product isolated after work-up was exclusively $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Br})_2$. However, when the reaction was repeated at -20°C , monitoring of the ^1H n.m.r. spectrum of the solution revealed the progressive appearance of multiplets in the δ 3.4–4.3 region, along with at least seven peaks in the region, near δ 0, associated with the protons of Me_3Si groups. After 6 h the only peaks in the latter region were singlets at δ 0.60, 0.40, and 0.36, in *ca.* 1:1:3 ratio, none of which corresponded to a peak from $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Br})_2$, which was, however, the only product obtained on work-up. We suspected that the initial products were those of addition of Br_2 to vinyl groups to give $\text{SiCHBrCH}_2\text{Br}$ linkages, which lose $\text{CH}_2=\text{CHBr}$ on work-up, and support for this view was provided by the observation that treatment of $\text{Me}_3\text{SiCH}=\text{CH}_2$ with Br_2 in CCl_4 at -20°C gave rise to multiplets in the δ 3.4–3.9 region similar to those observed in the reaction of (1); such reaction of $\text{Me}_3\text{SiCH}=\text{CH}_2$ with Br_2 is known to give the addition product $\text{Me}_3\text{SiCHBrCH}_2\text{Br}$, which can be isolated.⁴

We then turned to the reaction of the monovinyl species (2) with Br_2 under similar conditions and again the solution showed multiplets in the δ 3.4–4.3 range, along with singlets at δ 0.24 and 0.65, the three sets of signals having an integration ratio of 1:9:2; the data are consistent with the presence of $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{CHBrCH}_2\text{Br}$, but work-up gave only $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{Br}$ (δ_{H} 0.30 and 0.70). [The isolation of $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{Br}$ after treatment of $(\text{Me}_3\text{Si})_3\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)$ with Br_2 in refluxing CCl_4 has been reported previously.⁵]

When (1) was treated with a two molar proportion of ICl in CCl_4 at room temperature, < 5% of reaction took place during 6 h, but when a large excess of ICl was used conversion into $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Cl})_2$ was complete by the time (< 1 min) the ^1H spectrum could be recorded. Subsequently further reaction took place, to give $(\text{Me}_3\text{Si})\text{C}(\text{SiMe}_2\text{Cl})_3$ and $\text{C}(\text{SiMe}_2\text{Cl})_4$ by cleavage of $\text{Si}-\text{Me}$ bonds.⁶

Although addition products were detected only in the reactions with Br_2 , it is possible that similar intermediates were formed in the reactions with the other halogens but rapidly decomposed.

No reaction occurred when HBr was bubbled for 3 h through a solution of (1) in Et_2O at -80°C or CCl_4 at -20°C and the solution was then kept at room temperature for 2 h. Similarly, there was no reaction when HCl was bubbled for 3 h through a solution of (1) in CCl_4 at -20°C or Et_2O at -80°C (with the mixture then allowed to warm to room temperature) or under reflux. In contrast, when the HCl was bubbled through a

solution of (1) in CCl_4 containing a two molar proportion of AlCl_3 , all the starting material had disappeared within 5 min to give a mixture of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Cl})_2$, $(\text{Me}_3\text{Si})\text{C}(\text{SiMe}_2\text{Cl})_3$, and $\text{C}(\text{SiMe}_2\text{Cl})_4$ in *ca.* 10:85:5 ratio, and after 3 h only the tetrachloride was present. However, we subsequently found that the tetrachloride was similarly formed during 3 h when the passage of HCl was omitted. It has previously been shown that $(\text{Me}_3\text{Si})_4\text{C}$ reacts with $\text{AlCl}_3\text{-MeCOCl}^7$ or $\text{AlCl}_3\text{-Me}_3\text{SiCl}^8$ mixtures to give $\text{C}(\text{SiMe}_2\text{Cl})_4$, and in the light of our observation on (1) it seems likely that these conversions would take place on treatment of $(\text{Me}_3\text{Si})_4\text{C}$ with AlCl_3 alone.

Reaction with $\text{CF}_3\text{CO}_2\text{H}$.—Compound (1) reacted with $\text{CF}_3\text{CO}_2\text{H}$ during 4 h at 60°C apparently to give exclusively $(\text{Me}_3\text{Si})_3\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)(\text{SiMe}_2\text{O}_2\text{CCF}_3)$, as judged from the ^1H n.m.r. spectrum. [There must, however, have been a little undetected $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{O}_2\text{CCF}_3)_2$ present.] Monitoring by ^1H n.m.r. spectroscopy gave a good first-order plot with $t_{1/2}$ *ca.* 43 min. The reaction of the monovinyl compound (2) under similar conditions also gave a good first-order plot, with $t_{1/2}$ *ca.* 180 min. It thus appears that each of the Si-vinyl bonds in (1) is cleaved only about twice as readily as that in (2), and that anchimeric assistance plays no part. This is understandable if, as is likely, the rate-determining step is the initial protonation to give the $\text{SiCH}_2\text{CH}_2^+$ linkage.

The monotrifluoroacetate $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)(\text{SiMe}_2\text{O}_2\text{CCF}_3)$ was also found to react, but more slowly, with $\text{CF}_3\text{CO}_2\text{H}$ at 60°C ; the conversion into $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{O}_2\text{CCF}_3)_2$ was half-complete in *ca.* 14 h, and hence the monotrifluoroacetate is *ca.* 5 times less reactive than (2) and *ca.* 20 times less reactive than (1); the latter factor reduces to 10 after allowance for the presence of two Si-vinyl bonds in (1). It is possible that protonation of the carbonyl group in the monotrifluoroacetate results in some inhibition of protonation of the vinyl group.

It is noteworthy that the clean conversion of (1) into $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)(\text{SiMe}_2\text{O}_2\text{CCF}_3)$ could be of value in synthesis. This is because (1) can be readily obtained directly from $(\text{Me}_3\text{Si})_2\text{CCl}_2$, and $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)(\text{SiMe}_2\text{O}_2\text{CCF}_3)$ can be converted into a range of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{-CH}=\text{CH}_2)(\text{SiMe}_2\text{X})$ species, especially *via* the compound with $\text{X} = \text{OH}$.^{2,9}

No reaction took place when a solution of (1) or (2) in 2.0M-MeONa-MeOH was refluxed for six days. The compounds $(\text{Me}_3\text{Si})_4\text{C}$ and $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{OMe}$ are similarly inert under such conditions, whereas $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{H}$ is readily converted into $(\text{Me}_3\text{Si})_3\text{CH}$.¹⁰

Experimental

Solvents were dried as previously described. Mass spectra were determined by electron impact at 70 eV. The ^1H n.m.r. spectra refer to solutions in CCl_4 containing Me_2CO as lock and reference. For m.p. determinations samples were sealed in capillaries.

Preparation of (1).—(a) A 2.5M solution of BuLi in hexane (0.75 cm^3 , 1.9 mmol of BuLi) was added dropwise under dry nitrogen to a stirred solution of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)\text{Cl}$ (0.50 g, 1.8 mmol)² in THF (60 cm^3), Et_2O (8 cm^3), and pentane (3 cm^3), kept at -100°C . The mixture was stirred at -100°C for a further 1.5 h, then allowed to warm to -70°C , and $\text{Me}_2(\text{CH}_2=\text{CH})\text{SiCl}$ (0.25 cm^3 , 2.4 mmol) was added dropwise. The mixture was allowed to warm to room temperature and volatile materials were removed under vacuum. The residual solid was extracted with pentane, and the extract was filtered and evaporated to leave a solid, which was sublimed (100°C at

0.1 Torr) to give *bis*[dimethyl(vinyl)silyl]*bis*(trimethylsilyl)-methane (1) (0.35 g, 60%), m.p. 280°C (Found: C, 54.8; H, 11.0. $\text{C}_{15}\text{H}_{36}\text{Si}_4$ requires C, 54.9; H, 11.0%); δ_{H} 0.18 (18 H, s, SiMe_3), 0.26 (12 H, s, SiMe_2), and 5.46–6.62 (6 H, m, $\text{CH}=\text{CH}_2$); $\nu(\text{C}=\text{C})$ (in CCl_4) 1590 cm^{-1} ; m/z 313 (100%, $[\text{M} - \text{Me}]^+$), 301 (5, $[\text{M} - \text{CH}=\text{CH}_2]^+$), 225 (25, $[\text{M} - \text{Me}_4\text{Si} - \text{Me}]^+$), 213 (25, $[\text{M} - \text{Me}_3\text{SiCH}=\text{CH}_2 - \text{Me}]^+$), 201 (10, $[\text{M} - \text{Me}_2\text{Si}(\text{CH}=\text{CH}_2)_2]^+$), 155 (15), 141 (15), 129 (15), 85 (20, $[\text{Me}_2\text{-}(\text{CH}_2=\text{CH})\text{Si}]^+$), 73 (95, $[\text{Me}_3\text{Si}]^+$), and 59 (30, $[\text{Me}_2\text{HSi}]^+$).

(b) A 1.6M solution of BuLi in hexane (13.0 cm^3 ; 0.021 mol) was added dropwise under N_2 to a solution of $(\text{Me}_3\text{Si})_2\text{CCl}_2$ (4.6 g, 0.20 mol) in THF (60 cm^3), Et_2O (8 cm^3), and pentane (3 cm^3) kept at -100°C . The mixture was stirred at -100°C for a further 2 h then $\text{Me}_2(\text{CH}_2=\text{CH})\text{SiCl}$ (2.5 cm^3 , 0.024 mol), cooled to -80°C , was added dropwise. The mixture was subsequently allowed to warm to room temperature and volatile materials were removed under vacuum. The residue was extracted with pentane, the extract was filtered and evaporated, and some unchanged $(\text{Me}_3\text{Si})_2\text{CCl}_2$ was distilled off at 120°C at 20 Torr. The solid residue was recrystallized from MeOH to give (1) (2.64 g, 66%) based on the $\text{Me}_2(\text{CH}_2=\text{CH})\text{SiCl}$ taken.

It should be noted that, as mentioned in the main text, a very similar procedure, but with the BuLi solution cooled to -80°C before addition to the solution of $(\text{Me}_3\text{Si})_2\text{CCl}_2$ kept at -110°C (rather than at -100°C), was previously used to give $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)\text{Cl}$.²

Reactions of (1) with Halogens.—(a) No reaction was observed when a solution of (1) (0.33 g, 0.10 mmol) and I_2 (0.050 g, 0.20 mmol) in CCl_4 (20 cm^3) was kept at room temperature for 7 days then under reflux for 6 h.

(b) A solution of (1) (0.033 g, 0.10 mmol) and I_2 (0.25 g, 1.0 mmol) in CCl_4 (20 cm^3) was boiled under reflux. After 18 h the ^1H n.m.r. spectrum of the solution showed that (1), $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)(\text{SiMe}_2\text{I})$, and $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{I})_2$ were present in *ca.* 55:25:20 ratio (a mixture of authentic samples in this ratio had an identical spectrum), as judged from the signals from the $\text{SiMe}_2\text{CH}=\text{CH}_2$ and SiMe_2I protons. After five days only $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{I})_2$ was present. The solution was shaken with aqueous NaHSO_3 , then with water, then dried (MgSO_4) and evaporated. The residue was recrystallized from pentane to give $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{I})_2$ (0.035 g, 65%), m.p. 330°C (lit.,¹¹ $> 320^\circ\text{C}$) (Found: C, 25.4; H, 5.8. Calc. for $\text{C}_{11}\text{H}_{30}\text{I}_2\text{Si}_4$: C, 25.0; H, 5.7%); δ_{H} 0.45 (SiMe_3) and 1.18 (SiMe_2).

(c) A solution of (1) (0.15 g, 0.46 mmol) and Br_2 (7.0 mmol) in CCl_4 (20 cm^3) was refluxed for 2 h, cooled, shaken with aqueous NaHSO_3 , then water, dried (MgSO_4), and evaporated, to leave $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Br})_2$ (0.14 g, 71%), m.p. $> 330^\circ\text{C}$ (lit.,¹¹ $> 320^\circ\text{C}$) (Found: C, 30.7; H, 7.0. Calc. for $\text{C}_{11}\text{-H}_{30}\text{Br}_2\text{Si}_4$: C, 30.4; H, 6.9%); δ_{H} 0.40 (SiMe_3) and 0.88 (SiMe_2); m/z 419 (98%, $[\text{M} - \text{Me}]^+$), 267 (70, $[\text{M} - \text{Me}_3\text{-SiBr} - \text{Me}]^+$), 201 (15), 113 (10), 73 (100), and 59 (20).

(d) A solution of (1) (0.08 g, 0.024 mmol) and Br_2 (0.050 mmol) in CCl_4 (1 cm^3) in a closed n.m.r. tube was kept at -20°C . Multiplets progressively appeared in the δ 3.4–4.3 region, and at least seven peaks were present in the region (δ *ca.* 0–1) associated with Me_3Si protons. After 6 h there were only three peaks in the latter region, at δ 0.36, 0.40, and 0.60, in *ca.* 3:1:1 ratio, none of which corresponds to a peak from $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Br})_2$. The solvent was evaporated off, and the residue taken up in Et_2O . The solution was shaken with aqueous NaHSO_3 , then with water, dried (MgSO_4), and evaporated, to leave a solid which was shown by ^1H n.m.r. spectroscopy to be $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Br})_2$.

(e) A (1M) solution of ICl (0.92 mmol) in CCl_4 (0.92 cm^3) was added to a stirred solution of (1) (0.15 g, 0.46 mmol) in CCl_4 (20 cm^3) at room temperature. After 6 h the ^1H n.m.r. spectrum

indicated that *ca.* 95% of (1) was still present, along with a little $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Cl})_2$.

(f) When a solution of (1) (0.08 g, 0.024 mmol) and ICl (0.30 mmol) in CCl_4 (1 cm^3) was made up in a n.m.r. tube and was kept at 35 °C, the ^1H n.m.r. spectrum recorded within 1 min of mixing showed that complete conversion into $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Cl})_2$ had occurred. After 1 h the $(\text{Me}_3\text{Si})_{4-n}\text{C}(\text{SiMe}_2\text{Cl})_n$ compounds with n 2–4, respectively, were present in *ca.* 30:55:15 ratio, after 18 h those with n 3 and 4 were present in 1:1 ratio, and after three days only that with n 4 was present. The solution was shaken with aqueous NaHSO_3 then water, dried (MgSO_4), and then evaporated, to leave exclusively $\text{C}(\text{SiMe}_2\text{Cl})_4$ (0.60 g, 64%), with properties identical with those previously described.⁶

Reaction of (2) with Br_2 .—The procedure described under (d) above was repeated with (2) in place of (1); the signals from the starting material were replaced by signals at δ 0.24 (s), 0.65 (s), and 3.4–4.3 (m) in *ca.* 9:2:1 ratio. Work-up as in (d) above gave exclusively $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{Br}$, with properties identical with those of an authentic sample.

Treatment of (1) with HBr, HCl, and AlCl_3 .—(a) Hydrogen chloride was bubbled through a solution of (1) (0.30 g) in Et_2O (20 cm^3) at *ca.* –80 °C for 3 h, and the mixture was stirred at room temperature for a further 4 h. Removal of the solvent left only unchanged (1).

The same result was obtained when CCl_4 , initially at –20 °C, was used as solvent.

(b) There was a similar outcome when the HCl was passed for 7 h through a refluxing solution of (1) (0.30 g) in Et_2O or CCl_4 (20 cm^3).

(c) When HCl was bubbled through a refluxing solution of (1) (0.30 g, 0.91 mmol) and AlCl_3 (0.24 g, 1.8 mmol) in CCl_4 (20 cm^3), the ^1H n.m.r. spectrum of the solution showed progressive conversion of (1) into $(\text{Me}_3\text{Si})_{4-n}\text{C}(\text{SiMe}_2\text{Cl})_n$ species with n 2–4. After 5 min the compound with n 2 was exclusively present, after 45 min the compounds with n 2–4 were present in 10:85:5 ratio, and after 90 min only those with n 3 and 4 were present in *ca.* 1:1 ratio. After 3 h the solvent was evaporated off, and the residue extracted with pentane. Removal of the pentane from the extract left exclusively $\text{C}(\text{SiMe}_2\text{Cl})_4$, with properties identical with those described previously.⁶

(d) A solution of (1) (0.30 g, 0.91 mmol) and AlCl_3 (0.24 g, 1.8 mmol) in CCl_4 (20 cm^3) was refluxed for 3 h. Work-up as in (a) gave exclusively $\text{C}(\text{SiMe}_2\text{Cl})_4$.

(e) Hydrogen bromide was passed through a solution of (1) (0.30 g) in Et_2O (25 cm^3) for 3 h at –80 °C, and the mixture was then allowed to warm to room temperature during 2 h. Removal of the solvent left only unchanged (1).

A similar procedure but with CCl_4 , initially at –20 °C, as solvent gave the same result.

Reactions with $\text{CF}_3\text{CO}_2\text{H}$.—(a) Trifluoroacetic acid (1 cm^3) was added to (1) (0.03 g) dissolved in a drop (*ca.* 0.02 cm^3) of CCl_4 . The tube was capped, then placed in a bath at 60 °C, and

removed at intervals for recording of the ^1H n.m.r. spectrum. The heights of the singlets from the Me_3Si protons of (1) (δ 0.18) and the product (δ 0.31) were used to estimate the extents of reaction: a good first-order plot with $t_{\frac{1}{2}}$ 43 min was obtained up to >90% completion of the reaction. After 4 h the solvent was removed under vacuum and the residue shown by its ^1H n.m.r. spectrum, δ 0.31 (18 H, s), 0.37 (6 H), 0.64 (6 H, s), and 5.8–6.5 (3 H, m), to be $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)(\text{SiMe}_2\text{O}_2\text{CCF}_3)$, an authentic sample of which was available.

(b) In a similar procedure but with $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)(\text{SiMe}_2\text{O}_2\text{CCF}_3)$ in place of (1), the extents of reaction at various times were: 22%, 5 h; 50%, 14 h; 71%, 25 h; 95%, 60 h. After 72 h removal of the solvent left exclusively $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{O}_2\text{CCF}_3)_2$, m.p. 108 °C; δ_{H} 0.32 (18 H, s) and 0.65 (12 H, s); δ_{F} –74.1 p.p.m. The properties are in good agreement with those previously reported.¹²

(c) A procedure similar to that in (a) but with (2) in place of (1) gave a good first-order plot with $t_{\frac{1}{2}}$ 180 min, and the product was identified as $(\text{Me}_3\text{Si})_3\text{C}(\text{SiMe}_2\text{O}_2\text{CCF}_3)$.

Treatment of (1) and (2) with NaOMe – MeOH .—A solution of (1) (0.15 g) in 2M- NaOMe (20 cm^3) was kept under reflux for 6 days. Work-up gave only unchanged (1). A similar result was obtained with (2) in place of (1).

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