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STERICALLY-HINDERED ORGANOSILICON PERCHLORATES *

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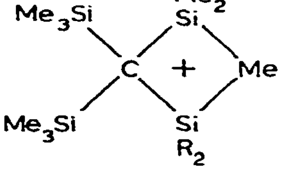
Summary

The perchlorates $(Me_3Si)_3C(SiMe_2OClO_3)$ and $(Me_3Si)_2C(SiPh_2Me)(SiMe_2ClO_3)$ have been obtained by treatment of the iodides $(Me_3Si)_3C(SiMe_2I)$ and $(Me_3Si)_3C(SiPh_2I)$, respectively, with $AgClO_4$ in CH_2Cl_2. The perchlorates react with MeOH to give the methoxides $(Me_3Si)_3C(SiMe_2OMe)$ and $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OMe)$, and with water in CH_3CN to give the corresponding hydroxides, while $(Me_3Si)_3C(SiMe_2OClO_3)$ reacts with $LiNMe_2/HNMe_2$ in ether to give the amide $(Me_3Si)_3CSiMe_2NMe_2$.

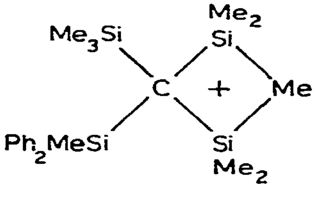
Introduction

Previous studies have demonstrated that the tris(trimethylsilyl)methylsilicon compounds, $(Me_3Si)_3CSiR_2X$, show a very high resistance towards attack of nucleophiles at silicon [1—4]. However, for X = I, substitution products can be obtained by treatment with electrophiles (such as silver or mercury(II) salts) in methanol [2]; such reactions appear to proceed through bridged-cations of type I, rearranged products of the type $(Me_3Si)_2C(SiR_2Me)(SiMe_2Y)$ commonly being obtained. In order to observe the effects of making X an exceptionally good leaving group, we have made the perchlorate $(Me_3Si)_3CSiMe_2OClO_3$ and the related compound $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OClO_3)$. (For an account of the chemistry of organosilicon perchlorates see ref. 5 and literature cited therein.)

In the account below the $(Me_3Si)_3C$ group is sometimes denoted by the symbol Tsi ("trisyl").



(I)



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Results and discussion

The perchlorate $TsiSiMe_2OClO_3$ was made very easily by treatment of the iodide $TsiSiMe_2I$ with $AgClO_4$ in CH_2Cl_2. A similar procedure with $TsiSiPh_2I$ gave exclusively the rearranged product $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OClO_3)$, presumably via the intermediate cation I with R = Ph_2.

$$(Me_3Si)_3CSiMe_2I + AgClO_4 \rightarrow (Me_3Si)_3CSiMe_2OClO_3$$

$$(Me_3Si)_3SiPh_2I + AgClO_4 \rightarrow (Me_3Si)_2C(SiPh_2Me)(SiMe_2OClO_3)$$

The perchlorates were found to undergo solvolysis readily in anhydrous methanol to give the corresponding methoxides, $TsiSiMe_2OMe$ and $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OMe)$.

$$(Me_3Si)_3CSiMe_2OClO_3 + MeOH \rightarrow (Me_3Si)_3CSiMe_2OMe$$

$$(Me_3Si)_2C(SiPh_2Me)(SiMe_2OClO_3) + MeOH \rightarrow (Me_3Si)_2C(SiPh_2Me)(SiMe_2OMe)$$

A preliminary account of a kinetic study of the methanolysis of $TsiSiMe_2ClO_3$ has appeared [6]; this indicated that the rate-determining step involves ionization, presumably to give the bridged cation I (R = Me). The two perchlorates also react with acetonitrile containing a little water to give the corresponding hydroxides $TsiSiMe_2OH$ and $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$. It is noteworthy that $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OClO_3)$ undergoes solvolysis without any migration of the Ph groups, although formation of a cationic intermediate analogous to I but with a bridging Ph group would not have been surprising; presumably either the intermediate cation II is involved, or a phenyl-bridged species analogous to I is formed but opens to give only the unrearranged product *.

$$(Me_3Si)_3CSiMe_2OClO_3 + H_2O \text{ (in } CH_3CN) \rightarrow (Me_3Si)_3CSiMe_2OH$$

$$(Me_3Si)_2C(SiPh_2Me)(SiMe_2OClO_3) + H_2O \text{ (in } CH_3CN)$$
$$\rightarrow (Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$$

The hydroxides $TsiSiMe_2OH$ and $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$ were also made from the iodides by treatment with silver perchlorate in wet acetonitrile. It seems likely that the hydroxides were produced directly from the initially produced ions (I and II) rather than through the perchlorates.

The perchlorates gave the corresponding hydride $TsiSiMe_2H$ and $(Me_3Si)_2C(SiPh_2Me)(SiMe_2H)$ upon reduction with $LiAlH_4$ in THF.

$$(Me_3Si)_3CSiMe_2OClO_3 + LiAlH_4 \rightarrow (Me_3Si)_3CSiMe_2H$$

$$(Me_3Si)_2C(SiPh_2Me)(SiMe_2OClO_3) + LiAlH_4 \rightarrow (Me_3Si)_2C(SiPh_2Me)(SiMe_2H)$$

The latter hydride was also made by similar reduction of the chloride $(Me_3Si)_2C(SiPh_2Me)(SiMe_2Cl)$. The perchlorate $TsiSiMe_2OClO_3$ also gave the first trisyl-

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* Since $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OClO_3)$ undergoes methanolysis more slowly than $(Me_3Si)_3CSiMe_2OClO_3$ [8], anchimeric assistance by Ph groups seems to be less than that by Me groups, and so a phenyl-bridged species is a less likely intermediate than II.

silicon amide, $TsiSiMe_2NMe_2$, in low yield, by treatment with $LiNMe_2/Me_2NH$ in ether.

$(Me_3Si)_3CSiMe_2OClO_3 + LiNMe_2/Me_2NH \rightarrow (Me_3Si)_3CSiMe_2NMe_2$

Treatment of the perchlorate $TsiSiMe_2OClO_3$ with n-BuLi did not give a Bu—Si bond. The product isolated after hydrolytic work-up was $TsiSiMe_2OH$; we did not investigate whether this was formed simply by hydrolysis of the perchlorate.

In associated studies two noteworthy observations were made, as follows:

(1) Attempts to convert the hydride $(Me_3Si)_2C(SiPh_2Me)(SiMe_2H)$ into the corresponding iodide by treatment with ICl were unsuccessful. Use of a 2/1 molar ratio of ICl to the hydride gave the chloride $(Me_3Si)_2C(SiPh_2Me)(SiMe_2Cl)$ in high yield, as expected [3,7], but with less than one equivalent of ICl only this chloride and unchanged hydride were obtained, and none of the expected iodide $(Me_3Si)_2C(SiPh_2Me)(SiMe_2I)$ was formed. We do not know why the reaction takes a different course from that followed by the various hydrides $TsiSiR_2H$ examined, all of which gave the iodide (without rearrangement) when less than 1 equivalent of ICl was used [3,7].

(2) Treatment of the acetate $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OAc)$ with $LiAlH_4$ in ether gave the hydroxide $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$ rather than the corresponding hydride. Presumably the severe steric hindrance to nucleophilic attack at silicon directs the reaction to the carbonyl group. It is unlikely that the hydroxide was formed during the hydrolytic work-up, since the acetate was recovered unchanged after treatment for 0.5 h under reflux with a mixture of THF (10 cm^3) and aqueous 1 *M* NaOH (5 cm^3).

Experimental

Reagents. The compounds $TsiSiMe_2I$, $TsiSiPh_2I$, and $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OAc)$ were made as previously described [1—3].

Silver perchlorate was dried for 18 h at 150°C under vacuum (ca. 1 mmHg). Methylene chloride was washed with 5% aqueous $NaHCO_3$, kept over anhydrous $CaCl_2$ for 24 h, then distilled and stored over a molecular sieve. "Wet" acetonitrile refers to the commercially-supplied solvent used without any treatment to remove water.

The ^1H NMR spectra were recorded at 60 MHz with solutions in CCl_4 containing CH_2Cl_2 as internal standard; δ values are in ppm.

Preparation of perchlorates *. (a) Powdered $AgClO_4$ (0.65 g, 0.003 mol) was added under dry nitrogen to a solution of $TsiSiMe_2I$ (1.0 g, 0.0024 mol) in CH_2Cl_2 (20 cm^3). The mixture was refluxed for 1 h, after which the ^1H NMR spectrum showed that none of the starting iodide remained. The solution was filtered, and the solvent evaporated under vacuum, and the residual solid was recrystallized from anhydrous pentane to give $TsiSiMe_2OClO_3$ (0.80 g, 86%). The sample taken for analysis (Found: C, 36.9; H, 8.9. $C_{12}H_{33}ClO_4Si_4$ calcd.: C, 37.0; H, 8.5%) was purified by sublimation (at 100°C/1 mmHg): The ^1H NMR spectrum gave peaks at δ 0.33 (s, 27H); 0.75 (s, 6H).

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* Although we have experienced no explosions with the perchlorates we nevertheless always handle them with appropriate precautions.

(b) A similar procedure starting from $TsiSiPh_2I$ gave $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OClO_3)$ (91%); m.p. 138—139°C, (Found: C, 51.3, H, 7.3. $C_{22}H_{37}ClO_4Si_4$ calcd.: C, 51.5; H, 7.3%); δ 0.30 (s, 18H); 0.54 (s, 6H); 1.01 (s, 3H), 7.3—8.1 (m, 10H).

Reactions of the perchlorates

(1) Methanolysis. (a) A solution of $TsiSiMe_2OClO_3$ (0.30 g) in a little CH_2Cl_2 (ca. 0.5 cm^3) was added to anhydrous MeOH (8 cm^3), and the mixture was kept at room temperature (ca. 22°C) for 3 h, during which a white solid separated. Extraction with hexane followed by drying (Na_2SO_4) and evaporation of the extract gave $(Me_3Si)_3C(SiMe_2OMe)$ (2.5 g, 86%) (authentic ^1H NMR spectrum [3]).

(b) A similar procedure starting from $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OClO_3)$ gave $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OMe)$ (90%) (authentic ^1H NMR spectrum [3]).

(2) Hydrolysis. To $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OClO_3)$ (0.30 g) was added wet CH_3CN (10 cm^3). The solution was kept at 50°C for 10 min, and the solvent was then evaporated off to leave $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$ (0.22 g, 88%), m.p. 137—138°C; ν(SiOH) (Nujol) 3640 (sh) and 3600—3200 cm^{-1} (br); δ 0.16 (s, 6H), 0.20 (s, 18H), 0.96 (s, 3H), 1.87 (br. s, 1H); 7.1—8.1 (m); the signal at 1.87 disappeared when the CCl_4 solution was shaken with D_2O. (Found: C, 61.0; H, 8.7. $C_{22}H_{38}OSi_4$ calcd.: C, 61.3; H, 8.9%).

(3) Reduction with $LiAlH_4$. (a) A solution of $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OClO_3)$ (0.30 g) in tetrahydrofuran (10 cm^3) was stirred with $LiAlH_4$ (0.30 g) at room temperature for 3 h. The usual work-up gave $(Me_3Si)_2C(SiPh_2Me)(SiMe_2H)$ (0.21 g, 88%) m.p. 119—120°C, ν(SiH) 2100 cm^{-1}; δ 0.15 (s, 18H), 0.23 (s, 6H), 0.93 (s, 3H), 4.89 (s, 1H), 7.1—8.0 (m, 10H) (Found: C, 63.8; H, 9.1. $C_{22}H_{38}Si_4$ calcd.: C, 63.7; H, 9.2%).

(b) A similar procedure starting from $TsiSiMe_2OClO_3$ gave $TsiSiMe_2H$ (91%), with properties identical to those described previously [3].

(4) Reaction with $LiNMe_2/Me_2NH$. A solution of n-BuLi (0.003 mol) in ether (2 cm^3) was treated with Me_2NH (2 cm^3) at —70°C. The solution was allowed to warm to 0°C, and treated with a solution of $TsiSiMe_2OClO_3$ (0.50 g, 0.0013 mol) in ether (5 ml). The mixture was allowed to warm to room temperature, and was then refluxed for 2.5 h. The solvent was then removed under vacuum, and the residue was warmed with hexane (10 cm^3). The hexane solution was filtered, and the solvent was removed to leave a semi-solid. This was pressed between filter papers to remove the liquid, and the crude solid was purified by two successive sublimations (80°C/1 mmHg) to give a white solid (0.12 g, 23%), m.p. 283—285°C; δ (CCl_4), 0.22 (s, 27H); 0.32 (s, 6H), 2.47 (s, 6H, NMe_2). (Found: C, 50.6; H, 11.4; N, 3.7. $C_{14}H_{39}NSi_4$ calcd.: C, 50.4; H, 11.7; N, 4.2%).

Several similar experiments all gave low yields. A liquid which was formed in substantial amount was not investigated.

(5) With n-BuLi. A solution of $TsiSiMe_2OClO_3$ (0.30 g, 0.78 mmol) in tetrahydrofuran (2 cm^3) was treated with n-BuLi (3 mmol) in tetrahydrofuran (2 cm^3) at —70°C. After 30 min the mixture was allowed to warm to room temperature, and kept at this temperature for 2 h. The usual hydrolytic work-up gave $TsiSiMe_2OH$ (0.18 g, 80%).

Preparation of hydroxides

(a) The iodide $TsiSiPh_2I$ (0.50 g, 0.9 mmol) was refluxed for 5 h with wet CH_3CN (15 cm^3) containing $AgClO_4$ (0.30 g, 1.4 mmol), after which the solution was filtered and the solvent evaporated off under vacuum. The residue was extracted with hexane (2 × 5 cm^3); and the extract was evaporated to leave a solid which was recrystallized from hexane to give the hydroxide $(Me_3Si)_2$-$C(SiPh_2Me)(SiMe_2OH)$ (0.20 g, 50%), m.p. 137—138°C, with spectra identical with those of the sample obtained as described above.

(b) A similar procedure starting from $TsiSiMe_2I$ gave $TsiSiMe_2OH$ (72%); ν(OH) 3670 (sharp) and 3600—3200 cm^{-1} (v.br); δ 0.43 (s, 27H), 0.49 (s, 6h), 1.40 (br, s, 1H); the singlet at δ 1.40 disappeared when the solution in CCl_4 was shaken for 20 min with D_2O. A sample for analysis was obtained by sublimation (110°C/1 mmHg) (Found: C, 46.8; H, 10.6. $C_{12}H_{34}OSi_4$ calcd.: C, 47.1; H, 11.1%).

Reactions of $(Me_3Si)_2C(SiPh_2Me)(SiMe_2X)$ (X = Cl or OAc) with $LiAlH_4$

(a) A solution of $(Me_3Si)_2C(SiPh_2Me)(SiMe_2Cl)$ (1.0 g, 2.2 mmol) was refluxed with $LiAlH_4$ (0.6 g, 16 mmol) in tetrahydrofuran (15 cm^3) for 4.5 h. (Longer refluxing gave a lower yield.) The mixture was added to ice, and hydrochloric acid was added to dissolve inorganic salts. Ether extraction following by drying ($MgSO_4$) and evaporation of the extract left a solid, which was recrystallized from methanol to give the hydride $(Me_3Si)_2C(SiPh_2Me)(SiMe_2H)$ with properties identical to those described above.

(b) The acetate $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OAc)$ (0.50 g, 1.1 mmol) was refluxed with $LiAlH_4$ (0.50 g, 13 mmol) in ether (20 cm^3) for 9 h. Work-up as above, culminating in the removal of the ether, gave the hydroxide $(Me_3Si)_2$-$C(SiPh_2Me)(SiMe_2OH)$ (0.35 g, 75%), with properties identical to those described above.

Reaction of $(Me_3Si)_2C(SiPh_2Me)(SiMe_2H)$ with ICl

(a) Reactions carried out in NMR tubes showed that when $(Me_3Si)_2$-$C(SiPh_2Me)(SiMe_2H)$ and ICl were taken in 1/2 molar ratio, the chloride $(Me_3Si)_2C(SiPh_2Me)(SiMe_2Cl)$ was formed quantitatively. With 1/1 to 2/1 mol ratios, only the chloride and unchanged hydride were present, and there was no evidence for formation of any silicon iodide.

(b) The isolation of the chloride $(Me_3Si)_2C(SiPh_2Me)(SiMe_2Cl)$ from a preparative scale reaction with 1/2 molar ratio of hydride to ICl has been described previously [7].

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