Preparation and Some Reactions of Compounds of the Type $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2X)$. Anchimeric Assistance by the Methoxy Group

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Because of anchimeric assistance by the γ-OMe group the compound $R_2C(SiMe_2OMe)(SiMe_2Cl)$ (**1**) ($R = SiMe_3$ throughout), in contrast to the closely related R_3CSiMe_2Cl, reacts readily with silver salts; thus reactions with AgY or $AgBF_4$ give the compounds $R_2C(SiMe_2OMe)(SiMe_2X)$ with X = ONO_2, NCO, $OCOCF_3$ OCOMe, OCOPh, $OSO_2C_6H_4Me$-*p*, or F. The anchimeric assistance is so great that even the hydride $R_2C(SiMe_2OMe)(SiMe_2H)$ reacts with silver salts; thus $AgOCOCF_3$ gives $R_2C(SiMe_2OMe)(SiMe_2OCOCF_3)$. The azide $R_2C(SiMe_2OMe)(SiMe_2N_3)$ was made by treatment of (**1**) with NaN_3 in $(MeOCH_2)_2$. Treatment of (**1**) with water in dioxane gives $R_2C(SiMe_2OMe)(SiMe_2OH)$ in the presence of Et_3N and $R_2C(SiMe_2OH)_2$ in its absence. Likewise reaction with CF_3CH_2OH gives $R_2C(SiMe_2OMe)(SiMe_2OCH_2CF_3)$ in the presence of Et_3N and $R_2C(SiMe_2OCH_2CF_3)_2$ in its absence. The bis(trifluoroacetate) $R_2C(SiMe_2OCOCF_3)_2$ reacts with MeOH more slowly than $R_2C(SiMe_2OMe)(SiMe_2OCOCF_3)$, indicating that the γ-$OCOCF_3$ provides less anchimeric assistance than the γ-OMe group.

It has been briefly reported that the γ-OMe group in the compound $R_2C(SiMe_2OMe)(SiMe_2Cl)$ (**1**) ($R = SiMe_3$ throughout this paper) provides powerful anchimeric assistance to the departure of the Cl^- in alcoholysis, the reaction apparently involving rate-determining ionization to give the methoxy-bridged cation (**2**);[1] thus (**1**) is $> 10^6$ times as reactive towards MeOH as the closely related compound $R_2C(SiMe_2Cl)$.[2] We describe below the preparations and some reactions of a range of compounds $R_2C(SiMe_2OMe)(SiMe_2X)$ required for a detailed study of such anchimeric assistance.

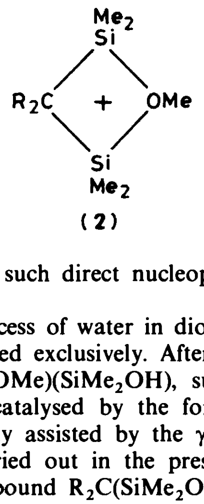
Results and Discussion

Compound (**1**), the starting material for most of the work described here, was usually made as previously described by treatment of $R_2C(SiMe_2OMe)Li$ (*cf.* ref. 3) with Me_2SiCl_2.[4] It was also obtained, however, *via* the hydride $R_2C(SiMe_2OMe)(SiMe_2H)$, which was made from $R_2C(SiMe_2OMe)Li$ and Me_2SiHCl; the hydride was treated with ICl to give (**1**). It is of interest that only the chloride (**1**) was isolated even when slightly less than 1 molar proportion of ICl was used, since R_3CSiMe_2H under the same conditions gives only the iodide R_3CSiMe_2I.[5,6] It is uncertain whether the chloride (**1**) is the initial product or comes from prior formation of the iodide and subsequent reaction of the latter.[7]

The chloride R_3CSiMe_2Cl does not react with silver salts under conditions in which the corresponding iodide reacts readily.[5] Because of the powerful anchimeric assistance by the OMe group, the chloride (**1**) also reacts readily with a range of silver salts, AgY, in CH_2Cl_2 or Et_2O, and the compounds $R_2C(SiMe_2OMe)(SiMe_2X)$ with X = ONO_2, NCO, $OCOCF_3$, OCOMe, OCOPh, or $OSO_2C_6H_4Me$-*p*, were obtained in this way. (The formation of the normal thiocyanate on reaction with AgSCN has been briefly reported.[8]) Use of $AgBF_4$ likewise gave the fluoride $R_2C(SiMe_2OMe)(SiMe_2F)$. So great is the effect of the OMe group that even the hydride $R_2C(SiMe_2OMe)(SiMe_2H)$ reacts with silver salts; thus with $AgOCOCF_3$ it rapidly gave the trifluoroacetate.

The azide $R_2C(SiMe_2OMe)(SiMe_2N_3)$ was obtained by treating (**1**) with NaN_3 in 1,2-dimethoxyethane; the reaction requires several hours under reflux because (**1**) is only a few times as reactive as $TsiSiMe_2Cl$ in such direct nucleophilic substitutions.[9]

$R_2C(SiMe_2OMe)(SiMe_2Cl)$
(**1**) ($R = SiMe_3$)



(**2**)

When (**1**) was treated with an excess of water in dioxane the diol $R_2C(SiMe_2OH)_2$ was formed exclusively. After the initial conversion into $R_2C(SiMe_2OMe)(SiMe_2OH)$, subsequent loss of the OMe group is catalysed by the formed hydrochloric acid and anchimerically assisted by the γ-OH group. When the reaction was carried out in the presence of Et_3N the methoxy-hydroxy compound $R_2C(SiMe_2OMe)(SiMe_2OH)$ was obtained. Treatment of (**1**) with CF_3CH_2OH likewise gave $R_2C(SiMe_2OMe)(SiMe_2OCH_2CF_3)$ in the presence of Et_3N but $R_2C(SiMe_2OCH_2CF_3)_2$ in its absence. The nitrate $R_2C(SiMe_2OMe)(SiMe_2ONO_2)$ reacted readily with MeOH at room temperature to give $R_2C(SiMe_2OMe)_2$, and with CF_3CH_2OH to give $R_2C(SiMe_2OCH_2CF_3)_2$.

The dimethoxide $R_2C(SiMe_2OMe)_2$ did not react with refluxing ethanol or aqueous acetone, but with the more acidic CF_3CH_2OH it gave $R_2C(SiMe_2OCH_2CF_3)_2$. The latter did not react with refluxing MeOH.

The chloride (**1**) reacted readily with CF_3CO_2H at room temperature to give $R_2C(SiMe_2OCOCF_3)_2$. When a solution of the latter in MeOH was kept at 60 °C, half of it had reacted after *ca.* 60 h. The methoxy trifluoroacetate $R_2C(SiMe_2OMe)(SiMe_2OCOCF_3)$ was markedly more reactive, half of it reacting in about 1 h, and conversion into $R_2C(SiMe_2OCOCF_3)_2$ being complete within 20 h; it is evident that under these conditions the γ-$OCOCF_3$ group supplies anchimeric assistance considerably less effectively than the γ-OMe group.

Experimental

The ^1H n.m.r. spectra were recorded (for solutions in CCl_4 containing CH_2Cl_2 as lock and reference) at 90 MHz with a

Perkin-Elmer R32 spectrometer. Unless otherwise indicated ^{19}F n.m.r. spectra were recorded at 84.6 MHz with the same spectrometer or at 75.4 MHz with a Bruker WP80 FT spectrometer for solutions in CCl_4 containing $CFCl_3$ as reference; negative shifts are upfield from $CFCl_3$. The i.r. spectra were recorded (for Nujol mulls between NaCl plates unless otherwise indicated) with a Perkin-Elmer 1574 spectrophotometer. All solvents were dried by standard methods.

Preparations of $R_2C(SiMe_2OMe)(SiMe_2X)$.—(*a*) X = H. A 1.6M-solution of Bu^{n}Li (10.6 mmol) in hexane (6.60 cm^3) was added dropwise at −110 °C to a stirred solution of $R_2C(SiMe_2OMe)Cl$[4] (3.0 g, 10.6 mmol) in a mixture of tetrahydrofuran (THF) (65 cm^3), Et_2O (3.0 cm^3), and n-pentane (3.0 cm^3). The mixture was stirred at −110 °C for 40 min then allowed to warm to −80 °C, and Me_2SiHCl (1.0 g, 0.0107 mol) was added dropwise. The mixture was allowed to warm to room temperature, volatile material was removed under vacuum, and the solid residue recrystallized from MeOH to give (*dimethylsilyl*)(*methoxydimethylsilyl*)*bis*(*trimethylsilyl*)*methane* (2.0 g, 62%), m.p. 195 °C; δ_H 0.16 (s, 18 H, $SiMe_3$), 0.24 (d, 6 H, $SiMe_2OMe$), 0.28 (s, 6 H, $SiMe_2H$), 3.38 (s, 3 H, OMe), and 3.96 (m, 1 H, SiH); ν(SiH) (Nujol) 2 100 cm^{-1}; *m/z* 291 (100%, $[M - Me]^+$), 217 (15, $[M - SiMe_2OMe]^+$), 201 (15, $[M - Me - SiMe_2HOMe]^+$), 187 (15), and 73 (50) (Found: 46.4; H, 11.4. $C_{12}H_{34}OSi_4$ requires C, 47.0; H, 11.2%).

(*b*) X = Br. A 1M-solution of Br_2 (2.1 mmol) in CCl_4 (2.1 cm^3) was added dropwise to a stirred solution of $R_2C(SiMe_2OMe)(SiMe_2H)$ (0.60 g, 1.9 mmol) in CH_2Cl_2 (4.0 cm^3). The mixture was stirred at room temperature for 20 min then the solvent was removed and the solid residue sublimed (100 °C at 0.5 Torr) to give (*bromodimethylsilyl*)(*methoxydimethylsilyl*)*bis*(*trimethylsilyl*)*methane* (0.51 g, 68%), m.p. 201 °C; δ_H 0.28 (s, 18 H, $SiMe_3$), 0.32 (s, 6 H, $SiMe_2OMe$), 0.77 (s, 6 H, $SiMe_2Br$), and 3.32 (s, 3 H, OMe); *m/z* 371, 369 (5%, $[M - Me]^+$), 290 (10, $[M - Me - Br]^+$), 275 (100, $[M - Me - MeBr]^+$), 201 (20), and 73 (30).

(*c*) X = Cl. A 1M-solution of ICl in CCl_4 (0.52 cm^3, 0.52 mmol) was added dropwise at room temperature to a stirred solution of $R_2C(SiMe_2OMe)(SiMe_2H)$ (0.20 g, 0.60 mmol) in CCl_4 (2.0 cm^3). The mixture was stirred for 10 min then evaporated, and the solid residue was sublimed (130 °C at 0.8 Torr) to give (chlorodimethylsilyl)(methoxydimethylsilyl)bis(trimethylsilyl)methane (**1**) (0.13 g, 60%), m.p. 295 °C; δ_H 0.27 (s, $SiMe_3$), 0.36 (s, Si*Me*$_2$OMe), 0.61 (s, $SiMe_2Cl$), and 3.32 (s, OMe). The physical constants are in good agreement with those reported for a sample obtained by a different method.[4]

(*d*) X = ONO_2. A solution of (**1**) (0.20 g, 0.60 mmol) in Et_2O (10 cm^3) was stirred with $AgNO_3$ (0.10 g. 0.6 mmol) at room temperature for 15 h. Filtration followed by removal of the solvent left a solid, which was sublimed (110 °C at 1 Torr) to give (*methoxydimethylsilyl*)(*dimethylnitro-oxysilyl*)*bis*(*trimethylsilyl*)*methane* (0.16 g, 75%), m.p. (sealed tube) 227 °C; δ_H 0.27 (s, 18 H, $SiMe_3$), 0.36 (s, 6 H, Si*Me*$_2$OMe), 0.62 (s, 6 H, $SiMe_2ONO_2$), and 3.38 (s, 3 H, OMe); *m/z* 352 ($[M - Me]^+$), 306 ($[M - Me - Me_2O]^+$), and 275 (35, $[M - Me - MeNO_3]^+$).

(*e*) X = NCO. A solution of (**1**) (0.30 g, 0.9 mmol) in CH_2Cl_2 (10.0 cm^3) was stirred at room temperature for 3 h with AgOCN (0.20 g, 1.3 mmol). Filtration and removal of the solvent left (*isocyanatodimethylsilyl*)(*methoxydimethylsilyl*)*bis*(*trimethylsilyl*)*methane* (0.25 g, 83%), m.p. 235 °C; δ_H 0.20 (s, 18 H, $SiMe_3$), 0.24 (s, 6 H, $SiMe_2$), 0.36 (s, 6 H, $SiMe_2$), and 3.38 (s, 3 H, OMe); ν(SiNCO) 2 280 cm^{-1}; *m/z* 332 (100%, $[M - Me]^+$), 275 (60), 228 (20), 217 (20), 201 (50), and 73 (65) (Found: C, 44.9; H, 10.1; N, 3.9. $C_{13}H_{33}NO_2Si_4$ requires C, 44.9; H, 9.6; N, 4.0%).

(*f*) X = $OCOCF_3$. (i) A solution of (**1**) (0.20 g, 0.6 mmol) in CH_2Cl_2 (10 cm^3) was stirred with $AgOCOCF_3$ (0.12 g, 0.6 mmol) for 30 min. The usual work-up left a residue, which was sublimed (100 °C at 0.5 Torr) to give (*methoxydimethylsilyl*)(*trifluoroacetoxydimethylsilyl*)*bis*(*trimethylsilyl*)*methane* (0.14 g, 60%), m.p. 195 °C; δ_H 0.20 (s, 18 H, $SiMe_3$), 0.28 (s, 6 H, Si*Me*$_2$OMe), 0.56 (s, 6 H, $SiMe_2OCOCF_3$), and 3.30 (s, 3 H, OMe); δ_F −128.0 (s); *m/z* 403 (100%, $[M - Me]^+$), 275 (70), 217 (10), 201 (15), and 73 (20) (Found: C, 40.5; H, 8.1. $C_{14}H_{33}F_3O_3Si_4$ requires C, 40.2; H, 8.0%).

(ii) A similar procedure but starting from $R_2C(SiMe_2OMe)(SiMe_2H)$ (0.31 g) and $AgOCOCF_3$ (0.23 g) in CH_2Cl_2 (20 cm^3), and with only 15 min stirring, gave the same product in 80% yield.

(*g*) X = OCOMe. A mixture of (**1**) (0.40 g), AgOCOMe (0.24 g), and CH_2Cl_2 was stirred at room temperature for 3 h. The usual work-up left a residue, which was sublimed (90 °C at 0.3 Torr) to give (*acetoxydimethylsilyl*)(*methoxydimethylsilyl*)*bis*(*trimethylsilyl*)*methane*, (0.32 g, 82%), m.p. 265 °C; δ_H 0.20 (s, 18 H, $SiMe_3$), 0.28 (s, 6 H, Si*Me*$_2$OMe), 0.48 (s, 6 H, $SiMe_2OCO$), 1.97 (s, 3 H, CH_3CO), and 3.36 (s, 3 H, OMe) (Found: C, 46.4; H, 10.1. $C_{14}H_{36}O_3Si_4$ requires C, 46.1; H, 9.95%).

(*h*) X = OCOPh. The procedure described under (*g*) was used, starting from AgOCOPh, but the residue after work-up was recrystallized from pentane, to give (*benzoyloxydimethylsilyl*)(*methoxydimethylsilyl*)*bis*(*trimethylsilyl*)*methane* (80%), m.p. 104 °C; δ_H 0.22 (s, 18 H, $SiMe_3$), 0.27 (s, 6 H, Si*Me*$_2$OMe), 0.57 (s, 6 H, $SiMe_2OCO$), 3.34 (s, 3 H, OMe), and 7.42—8.10 (m, 5 H, C_6H_5); *m/z* 411 (20%, $[M - Me]^+$), 307 (20), 275 (5), 105 (100, $[PhCO]^+$), 77 (30, $[Ph]^+$), and 73 (20) (Found: C, 53.6; H, 9.1. $C_{19}H_{38}O_3Si_4$ requires C, 53.5; H, 8.9%).

(*i*) X = F. A solution of (**1**) (0.40 g, 1.2 mmol) in CH_2Cl_2 (20 cm^3) was stirred with $AgBF_4$ (0.25 g, 1.3 mmol) for 30 min at room temperature. The usual work-up, culminating in sublimation (100 °C at 0.2 Torr), gave (*fluorodimethylsilyl*)(*chlorodimethylsilyl*)*bis*(*trimethylsilyl*)*methane* (0.33 g, 86%), m.p. 273 °C; δ_H 0.20 (s, 18 H, $SiMe_3$), 0.25 (s, 6 H, Si*Me*$_2$OMe), 0.35 (d, 6 H, $SiMe_2F$), and 3.37 (s, 3 H, OMe); $\delta_F(CDCl_3)$ −144.8 (m, *J* 7.3 Hz); *m/z* 309 (100%, $[M - Me]^+$), 221 (20), 217 (70) $[M - Me - Me_3SiF]^+$, 205 (45), 201 (60), 187 (35), and 73 (70).

(*j*) X = $OSO_2C_6H_4Me$-*p*. A mixture of (**1**) (0.35 g, 1.0 mmol), $AgOSO_2C_6H_4Me$-*p* (0.30 g, 1.0 mmol), and CH_2Cl_2 (20 cm^3) was stirred at room temperature for 4 h. The usual work-up left a residue, which was recrystallized from n-pentane to give (*methoxydimethylsilyl*)(p-*tolylsulphonyloxydimethylsilyl*)*bis*(*trimethylsilyl*)*methane* (0.35 g, 71%), m.p. 97 °C; δ_H 0.16 (s, 18 H, $SiMe_3$), 0.24 (s, 6 H, Si*Me*$_2$OMe), 0.62 (s, 6 H, $SiMe_2OSO$), 2.45 (s, 3 H, *p*-Me), 3.33 (s, 3 H, OMe), and 7.30—7.80 (m, 4 H, C_6H_4) (Found: C, 47.6; H, 8.4. $C_{19}H_{40}O_4SSi_4$ requires C, 47.9; H, 8.4%).

(*k*) X = N_3. A mixture of (**1**) (0.40 g, 1.3 mmol), NaN_3 (0.86 g, 13.2 mmol), and 1,2-dimethoxyethane (10 cm^3) was boiled under reflux for 6 h. Addition of water followed by extraction with n-hexane and washing, drying, and evaporation of the extract left a solid, which was sublimed (100 °C at 0.4 Torr) to give (*azidodimethylsilyl*)(*methoxydimethylsilyl*)*bis*(*trimethylsilyl*)*methane* (0.24 g, 60%), m.p. 270 °C; δ_H 0.23 (s, 18 H, $SiMe_3$), 0.31 (s, 6 H, Si*Me*$_2$OMe), 0.44 (s, 6 H, $SiMe_2N_3$), and 3.40 (s, 3 H, OMe); ν(SiN_3) 2 060 cm^{-1}; *m/z* 332 (15%, $[M - Me]^+$), 305 (20, $[M - N_3]^+$), 275 (10), and 73 (100) (Found: C, 42.2; H, 10.0. $C_{15}H_{33}N_3OSi_4$ requires C, 42.0; H, 9.6%).

(*l*) X = OH. A solution of (**1**) (0.4 g) in a mixture of dioxane (10 cm^3), water (1 cm^3), and Et_3N (1 cm^3) was stirred at room temperature for 36 h. The solvent was removed and the residue was extracted with n-pentane. The extract was filtered and evaporated, and the residue was sublimed (70 °C at 0.1 Torr) to give (*hydroxydimethylsilyl*)(*methoxydimethylsilyl*)*bis*(*trimethylsilyl*)*methane* (0.32 g, 84%), m.p. 265 °C; δ_H 0.23 (s, 18 H, $SiMe_3$), 0.30 (s, 6 H, $SiMe_2$), 0.32 (s, 6 H, $SiMe_2$), 1.33 (br s, 1 H, OH), and 3.40 (s, 3 H, OMe); ν(OH) (CCl_4) 3 700 (sharp) and 3 700—3 200 cm^{-1}; *m*/*z* 307 (35%, $[M - Me]^+$), 291 (30, $[M - OMe]^+$), 275 (60), 187 (20), 73 (100), and 59 (40, $[SiMe_2H]^+$) (Found: C, 44.3; H, 10.4. $C_{12}H_{34}O_2Si_4$ requires C, 44.7; H, 10.6%).

(*m*) X = OCH_2CF_3. A mixture of (**1**) (0.35 g), dioxane (5 cm^3), CF_3CH_2OH (2 cm^3), and Et_3N (1 cm^3) was stirred at room temperature for 24 h. Work-up as in (*l*) (with sublimation at 90 °C at 0.1 Torr) gave (*methoxydimethylsilyl*)(2,2,2-*trifluoroethoxydimethylsilyl*)*bis*(*trimethylsilyl*)*methane* (0.030 g, 72%), m.p. 204 °C; δ_H 0.19 (s, 18 H, $SiMe_3$), 0.25 (s, 6 H, $SiMe_2$), 0.27 (s, 6 H, $SiMe_2$), 3.25 (s, 3 H, OMe), and 3.65 (q, 2 H, CH_2CF_3); δ_F −75.9 (t, *J* 8.7 Hz); *m*/*z* 389 (100%, $[M - Me]^+$), 357 (10, $[M - Me - MeOH]^+$), 309 (25), 291 (10), 275 (30), 217 (15), 187 (10), and 73 (25).

Reactions of $R_2C(SiMe_2OMe)(SiMe_2X)$.—(*a*) A solution of (**1**) (0.40 g) in CF_3CH_2OH (10 cm^3) was stirred at room temperature for 1 h. Removal of the solvent left *bis*-(2,2,2-*trifluoroethoxydimethylsilyl*)*bis*(*trimethylsilyl*)*methane* (0.43 g, 77%), m.p. 67 °C; δ_H 0.22 (s, 18 H, $SiMe_3$), 0.32 (s, 12 H, $SiMe_2$), 3.70—4.01 (m, 4 H, CH_2); δ_F −76.0 (t); *m*/*z* 457 (10%, $[M - Me]^+$), 358 (10, $[M - Me - OCH_2CF_3]^+$), and 73 (100) (Found: C, 38.5; H, 7.4. $C_{15}H_{34}F_6O_2Si_4$ requires C, 38.1; H, 7.2%).

(*b*) A solution of (**1**) (0.20 g) in CF_3CO_2H (8 cm^3) was kept at room temperature for 20 min. Removal of the solvent under vacuum left $R_2C(SiMe_2OCOCF_3)_2$, m.p. 109 °C; δ_H 0.32 (s, 18 H, $SiMe_3$) and 0.64 (s, 12 H, $SiMe_2$); δ_F −124.0 (s). The properties agree well with those previously reported.[10]

(*c*) A solution of $R_2C(SiMe_2OMe)(SiMe_2ONO_2)$ (0.050 g) in a mixture of MeOH (5.0 cm^3) and CH_2Cl_2 (1.0 cm^3) was kept at 30 °C for 5 min. Evaporation under vacuum left exclusively $R_2C(SiMe_2OMe)_2$.

(*d*) A solution of $R_2C(SiMe_2OMe)(SiMe_2ONO_2)$ (0.05 g) in a mixture of CF_3CH_2OH (5 cm^3) and CH_2Cl_2 (1 cm^3) was kept at room temperature for 15 min. Evaporation under vacuum left exclusively $R_2C(SiMe_2OCH_2CF_3)_2$.

(*e*) A solution of $R_2C(SiMe_2OMe)(SiMe_2OCOCF_3)$ (0.05 g) in MeOH (5 cm^3) was kept at 60 °C. Monitoring of the ^1H n.m.r. signal at δ 0.16 ($SiMe_3$) showed that the reaction was *ca*. 54% complete in 1 h and complete in 24 h. Evaporation under vacuum left exclusively $R_2C(SiMe_2OMe)_2$.

(*f*) A solution of $R_2C(SiMe_2OMe)_2$ (0.20 g) in a mixture of water (1 cm^3) and acetone 9 cm^3) was boiled under reflux for 8 h. Removal of the solvent left only starting material. Refluxing for 15 h in EtOH gave a similar result.

(*g*) A solution of $R_2C(SiMe_2OMe)_2$ (0.15 g) in CF_3CH_2OH (10 cm^3) was boiled under reflux for 3 h. Removal of the solvent under vacuum left exclusively $R_2C(SiMe_2OCH_2CF_3)_2$.

Reactions of $R_2C(SiMe_2X)_2$.—(*a*) A solution of $R_2C(SiMe_2OCOCF_3)_2$ (0.06 g) in MeOH (5 cm^3) was kept at 60 °C, and samples were withdrawn periodically for ^1H n.m.r. spectroscopy. Half the starting material had disappeared in *ca*. 65 h. The product was not identified.

(*b*) A solution of $R_2C(SiMe_2OCH_2CF_3)_2$ (0.15 g) in MeOH (10 cm^3) was boiled under reflux for 15 h. Removal of the solvent left only starting material.

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