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POTASSIUM FLUORIDE ACTIVATED ALCOHOLYSIS OF HINDERED SILIRANES

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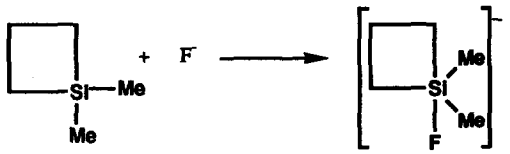
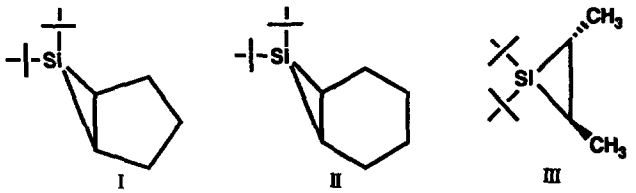
Abstract
The rate of alcoholysis of 1,1-di-*t*-butylsiliranes is significantly accelerated in the presence of 10% KF and still further enhanced by the addition of 1% 18-crown-6. A pentacoordinate siliconate is proposed as the intermediate responsible for the observed rate increases.

In the past few years there have been several reports on the use of fluoride to enhance the reactivity of organosilanes.[1,2] Typically, the organosilane is heavily substituted with electron withdrawing groups. In 1981, DePuy *et al.* reported the formation of a siliconate from the reaction of silacyclobutane with F^-, in a flowing afterglow system.[3]



The affinity of fluoride for the silacyclobutane was attributed to the relief of strain upon formation of the five coordinate siliconate. In solution, solvent induced isomerization and nucleophilic substitution of halosilacyclobutanes involving pentacoordinate intermediates have been described.[4,5] Corriu *et al.* have also studied the influence of angle strain of cyclic silanes on the stereochemistry of nucleophilic displacement reactions involving pentacoordinate intermediates.[6] To the best of our knowledge there are no reports in the literature on the reactions of fluoride ion with the most strained cyclosilanes, siliranes.

We have observed that siliranes I, II and III are highly reactive towards oxgen and water although less so than



I II III

previously described siliranes. Towards alcohols, I - III are slow to react. For example, I requires 20 hours of reflux conditions for butanol to produce the ring opened product in 12% yield. In contrast, the addition of 10 mol % of KF reduces the conditions to one hour of stirring and the yield increases to 70%. When 1% 18-crown-6 is used in combination with 10% KF a 79% yield of product is obtained in 15 min at room temperature. Our results are summarized in the Table.

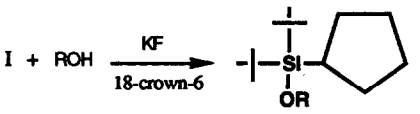
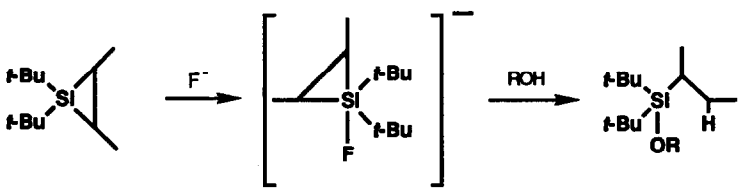


Table Potassium Flouride Activated Alcoholysis of Siliranes

Conditions	Alcohol	I	II	III
Control	MeOH	4 h (71%)[a]	12 h (75%)[a]	180°, 3 h (91%)[b]
	n-BuOH	20 h reflux (12%)	48 h reflux (8%)	180°, 3 h (90%)[b]
	cyclohexanol	100°, 6 h (74%)[b]	100°, 3 h (15%)[b]	180°, 5 h (86%)[b]
10% KF	MeOH	5 min (85%)[a]	5 min (95%)[a]	10 min (82%)[a]
	n-BuOH	1 h (70%)[a]	2-3 h (58%)[a]	10 h (65%)[a]
	cyclohexanol	21 h reflux (30%)	26 h reflux (34%)	80°, 40 h (21%)[b]
10% KF +	n-BuOH	15 min (79%)[a]	45 min (80%)[a]	6 h, (83%)[a]
1% 18-C-6	cyclohexanol	30 min reflux (95%)	35 min reflux (95%)	45 min reflux (92%)

All yields are GC yields. [a] Stirring at room temperature. [b] Heating in a sealed tube.

Presumably this catalytic process involves rapid coordination of fluoride to the siliranes forming a pentacoordinate species which facilitates attack of silicon by the alcohol.[7]



The ease with which these bulky groups can be placed on alcohols suggest that hindered siliranes may be useful precursors to very durable protecting groups for a variety of functionalities. We are exploring that possibility and will report our results in due course.

General procedure

A solution consisting of 5 mmol of alcohol and 10 mol% KF was placed in a 10 mL round bottom flask equipped with a N_2 inlet, rubber stopper, stirbar, 2 mL THF. To this solution 1mmol of silirane was added and stirred. The products were isolated by preparative GLC. The yields were calculated using an internal standard(decane).

***sec*-Butyldi-*t*-butylmethoxysilane.**The compound was identified by comparing with an authentic sample.[8]

Cyclopentyldi-*t*-butylmethoxysilane

^{1}H NMR (C_6D_6) δ 3.47 (3H, s), 1.55-1.9 (9H, m), 1.27(18H, s); ^{13}C NMR (C_6D_6) δ 52.65 (O-CH_3), 29.7 (cyclopentyl), 29.06 (CH_3, *t*-Bu), 27.02, 24.78 (cyclopentyl), 22.39 (*t*-Bu); MS, m/e (relative intensity) 242 (M^+, 1.39), 185 (M^+-57, 52.7); Anal. Calcd. for $C_{14}H_{30}SiO$: C, 69.35; H, 12.47. Found: C, 69.33; H,12.61.

Cyclohexyldi-*t*-butylmethoxysilane:

^{1}H NMR (C_6D_6) δ 3.45(3H, s), 1.7-2.0 (5H, m), 1.17-1.45 (5H, m), 1.14 (18H, s), 1.0 (1H, m); ^{13}C NMR (C_6D_6) δ 52.25 (O-CH_3), 29.5, 29.4 (cyclohexyl), 29.25 (CH_3, *t*-Bu), 27.75, 22.65 (cyclohexyl), 22.35 (*t*-Bu); MS, m/e (relative intensity) 256 (M^+, 0.137), 199 (M^+-57, 6.8); Anal. Calcd. for $C_{15}H_{32}SiO$: C, 70.24; H,12.57. Found: C, 70.08; H, 12.70.

***sec*-Butyldi-*t*-butyl-*n*-butoxysilane**

^{1}H NMR (C_6D_6) δ 3.64 (2H, t), 1.86 (1H, m), 1.43-1.51 (2H, m), 1.46-1.4 (2H, m), 1.16-1.27 (2H, m), 1.13 (3H, d), 1.09-1.1 (18H, 2s), 0.97 (3H, t), 0.86 (3H, t); ^{13}C NMR (C_6D_6) δ 63.76 (O-CH_2), 35.48 (*n*-butyl), 29.41, 29.3 (CH_3, *t*-Bu), 25.9, 22.41 (*sec*-butyl), 22.3, 21.3 (*t*-Bu), 19.42 (*n*-butyl), 14.93, 14.25 (*sec*-butyl), 14.1 (*n*-butyl); MS, m/e (relative intensity) 215 (M^+-57, 17.065); Anal. Calcd. for $C_{16}H_{36}SiO$: C, 70.51; H, 13.31. Found: C, 70.69; H, 13.41.

Cyclopentyldi-*t*-butyl-*n*-butoxysilane

^{1}H NMR (C_6D_6) δ 3.71 (2H, t), 1.7-1.9 (13H, m), 1.11 (18H, s), 0.91 (3H, t); ^{13}C NMR (C_6D_6) δ 64.24 (O-CH_2), 35.59 (*n*-butyl), 29.85 (cyclopentyl), 29.14 (CH_3, *t*-Bu), 27.05, 25.07 (cyclopentyl), 22.44 (*t*-Bu), 19.45, 14.12 (*n*-butyl); MS, m/e (relative intensity) 227 (M^+-57, 16.475); Anal. Calcd. for $C_{17}H_{36}SiO$: C, 71.75; H, 12.75. Found: C, 71.9; H, 12.45.

Cyclohexyldi-*t*-butyl-*n*-butoxysilane

^{1}H NMR (C_6D_6) δ 3.63 (2H, t), 1.61-1.8 (5H, m), 1.25-1.44 (5H, m), 1.1-1.2 (4H, m), 0.91 (s, 18H), 0.83 (1H, m), 0.78 (3H, t); ^{13}C NMR (C_6D_6) δ 63.86 (O-CH_2), 35.53 (*n*-butyl), 29.65 (cyclohexyl), 29.24 (CH_3, *t*-Bu), 27.62, 26.99, 22.35 (cyclohexyl), 19.42, 14.09 (*n*-butyl); MS, m/e (relative intensity) 298 (M^+, 0.4), 241 (M^+-57, 89.01); Anal. Calcd. for $C_{18}H_{38}SiO$: C, 72.41; H, 12.83. Found: C, 72.38; H, 12.97.

Cylcohexyl di-*t*-butylcyclopentylsilylether

^{1}H NMR (C_6D_6) δ 3.83 (1H, m), 1.55-1.95 (10H, m), 1.3-1.5 (5H, m), 1.15-1.25 (4H, m), 1.14 (18H, s); ^{13}C NMR (C_6D_6) δ 70.98 (O-CH), 36.13 (cyclohexyl), 29.23 (CH_3, *t*-Bu), 26.96, 26.11, 25.75, 23.88, 22.35 (cyclopentyl and cyclohexyl); MS, m/e (relative intensity) 253 (M^+-57, 11.4); Anal. Calcd. for $C_{19}H_{38}SiO$: C,73.47; H, 12.33. Found: C, 73.71; H, 12.39.

Cyclohexyl *sec*-butyldi-*t*-butylsilylether

^{1}H NMR (C_6D_6) δ 3.84 (1H, m), 1.95 (1H, m), 1.65-1.75 (5H, m), 1.22-1.5 (7H, m), 1.18 (3H, d), 1.15 (18H, s), 0.99 (3H, t); ^{13}C NMR (C_6D_6) δ 71.14 (O-CH), 36.15 (cyclohexyl), 29.41 (CH_3, *t*-Bu), 26.07, 23.91 (cyclohexyl) 22.54, 22.32, 15.14, 14.26 (*sec*-butyl); MS, m/e (relative intensity) 241 (M^+-57, 0.146); Anal. Cald. for $C_{18}H_{38}SiO$: C, 72.41; H, 12.83. Found: C, 72.41; H, 12.74.

Cyclohexyl di-*t*-butylcyclohexylsilylether

^{1}H NMR (C_6D_6) δ 3.96 (1H, m), 1.2-2.0 (21H, m), 1.5 (18H, s); ^{13}C NMR (C_6D_6) δ 71.08 (O-CH), 36.15, 30 (cyclohexyl), 29.27 (CH_3, *t*-Bu), 28.26, 27.59, 26.08, 23.92, 22.31 (cyclohexyl); MS, m/e (relative intensity) 324 (M^+, 0.169), 267 (M^+-57, 37.425); Anal. Calcd. For $C_{20}H_{40}SiO$: C, 73.9; H, 12.42. Found: C, 74.09; H, 12.26.

References

[1] Corriu, R. J. P.; Perz, R.; Reye, C. *Tetrahedron* **1983**, *39*, 999.
[2] Goldberg, Y.; Abele, E.; Shymanska, M.; Lukevics, E. *J. Organomet. Chem.* **1989**, *372*, C9.
[3] Sullivan, S. A.; DePuy, C. H.; Damrauer, R. *J. Am. Chem. Soc.* **1981**, *103*, 480.
[4] McKinnie, B. G.; Cartledge, F. K. *J. Organomet. Chem.* **1976**, *104*, 407.
[5] Dubac, J.; Mazerolles, P. Serres, B. *Tetrahedron* **1974**, *30*, 759.
[6] Corriu, R.; Guerin, C. *J. Organomet. Chem.* **1980**, *195*, 261.
[7] For a review of pentacoordinate silicon see Corriu, R. J. P.; Young, J. C. in *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1989, Ch 20.
[8] Boudjouk, P.; Samaraweera, U.; Sooriyakumaran, R.; Chrusciel, J.; Anderson,K.R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1355.

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