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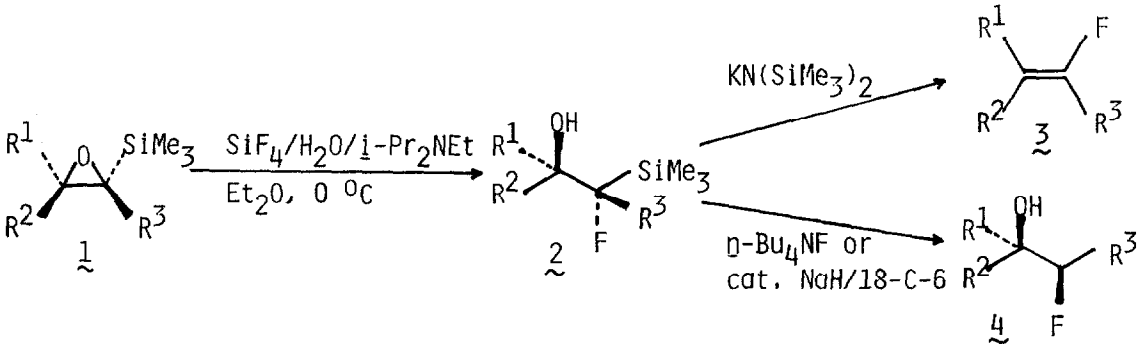
REGIOSPECIFIC RING OPENING OF α,β-EPOXYSILANES WITH SILICON TETRAFLUORIDE AND APPLICATION TO THE SYNTHESIS OF FLUOROALKENES

Makoto Shimizu and Hirosuke Yoshioka
The Institute of Physical and Chemical Research (RIKEN)
Wako, Saitama 351-01, Japan

Summary: α,β-Epoxysilanes undergo the ring opening-fluorination with silicon tetrafluoride in the presence of diisopropylethylamine and water to give β-fluoro-β-silyl alcohols specifically, and the subsequent olefination with potassium hexamethyldisilazide affords fluoroalkenes in good yield.

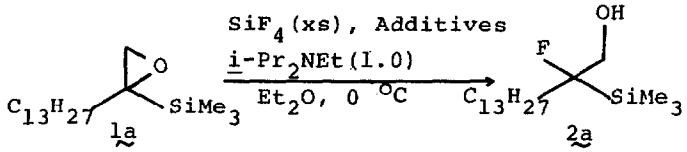
Although α,β-epoxysilanes are versatile intermediates for the specific synthesis of carbonyl compounds and olefins via β-hydroxysilanes,[1] the use as a substrate for the ring opening-fluorination appears to be difficult due to the strong affinity between silicon and fluoride anion, *i. e.*, desilylation may occur concomitantly.[2]

We have recently introduced a new fluorination system utilizing silicon tetrafluoride modified with certain additives and this system has proved to be a mild and selective tool for the ring openig-fluorination of epoxides.[3] In the present study, we have found that silicon tetrafluoride effects the ring opening-fluorination of α,β-epoxysilanes to produce β-fluoro-β-silyl alcohols without eliminating the silicon moiety, and the subsequent treatment with potassium hexamethyldisilazide leads to a new selective synthesis of fluoroalkenes.

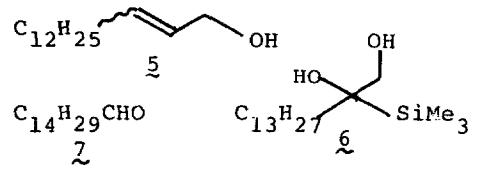


We initially attempted the ring opening-fluorination of α,β-epoxysilane **1a** with a series of fluorination agents: $Et_3N \cdot 3HF$ did not effect the ring opening, whereas with $(HF)_n \cdot Py$, $BF_3 \cdot Et_2O$, or KHF_2, the reaction gave the desilylated products (**5**, **7**) or the diol (**6**) and no fluorohydrin (**2a**) was obtained. In contrast to these reagents, SiF_4 with certain additives effects the selective ring opening-fluorination (see Table 1), where the use of H_2O (4.0 eq) and *i*-Pr_2NEt (1.0 eq) was crucial for the best yield (entry 3). The SiF_4/*n*-Bu_4NF system that worked well with silicon-free epoxides[3] was less effective due to the cleavage of the Si-C bond with fluoride anion.[2] A variety of α,β-epoxysilanes was transformed into fluorohydrins (see Table 2).

Table 1. Ring Opening-Fluorination of α,β-Epoxysilanes with SiF_4

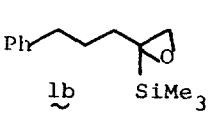
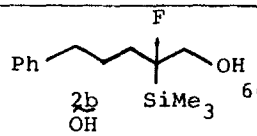
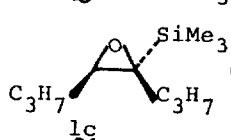
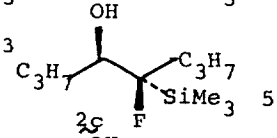
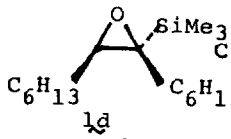
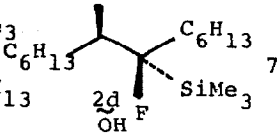
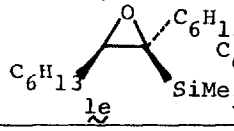
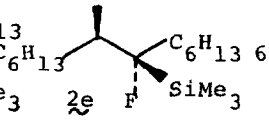
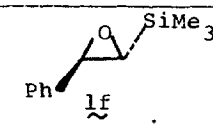
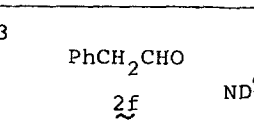
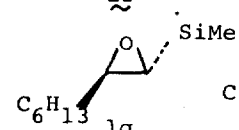
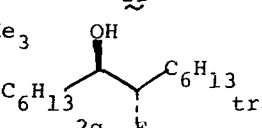
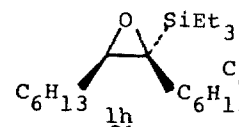
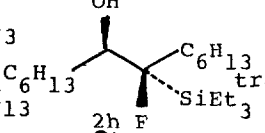


Entry	Additive	(equiv.)	2a (%yield)[a]
1	H_2O	(1.0)	31
2	H_2O	(2.0)	50
3	H_2O	(4.0)	80
4	n-Bu_4NF	(1.7)	50



[a]Isolated yield.

Table 2. Preparation of β-Fluoro-β-silyl Alcohols[a]

Entry	Epoxysilane	Product	(%yield)[b]
1			66
2			58
3			70
4			61
5			ND[c]
6			trace
7			trace

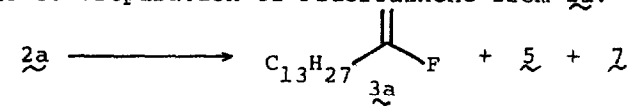
[a]The reaction was carried out under the conditions used for the entry 3 of Table 1. [b]Isolated yield. [c]Not determined.

The 1,1-disubstituted and 1,1,2-trisubstituted oxiranes (entries 1--4) gave the β-fluoro-β-silyl alcohols in fair to good yields, whereas the 1,2-disubstituted oxiranes (entries 5 and 6) practically did not afford the fluorohydrins. The oxirane having triethylsilyl group (entry 7) underwent ring opening-fluorination sluggishly, indicating that the trimethylsilyl substituent was essential in the present reaction. The fluorine atom was regiospecifically introduced into the carbon bearing the trimethylsily group. The stereochemical outcome was examined with **1d** and **1e** (entries 3 and 4), and the reaction was found to proceed stereospecifically to give the *trans*-opened fluorohydrins (**2d**, **2e**) in good yield.[4]

Next, the Peterson-type olefination[5] was examined with the fluorohydrin (**2a**) (see Table 3). In strong contrast to the fluorine-free analogues, $BF_3 \cdot Et_2O$ or H_2SO_4 did not effect the olefination but the rearranged allylic alcohol (**5**) and/or aldehyde (**7**) was obtained in each case. An intriguing behavior of **2a** was revealed under basic conditions. Treatment of **2a** with

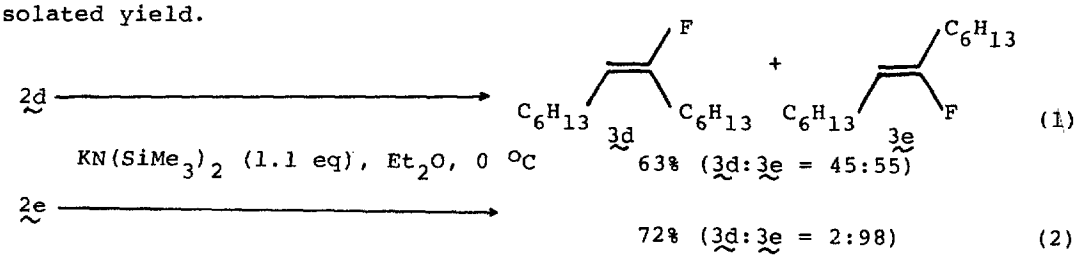
potassium hexamethyldisilazide gave the fluoroalkene (3a) in good yield, and the cyclization regenerating an α,β-epoxysilane was not observed, showing a distinct difference from β-bromo(or chloro)-β-silyl alcohols that readily underwent epoxidation upon treatment with bases.[6] The olefination proceeded stereoselectively with *syn*-silyl alcohol (2e), giving 3e predominantly (see eq. 2), whereas the *anti*-isomer (2d) gave a mixture of 3d and 3e in a 45:55 ratio (eq. 1).[7] This may be explained by a steric hindrance arising from two hexyl groups in the *anti*-isomer (2d) against *syn*-elimination, whereas the sterically preferred conformation with the *syn*-isomer (2e) allows the stereoselective olefination.[8,9]

Table 3. Preparation of Fluoroalkene from 2a.



Entry	Reagent (eq)	Temp (°C)	Solv.	3a (%)[a]	5 (%)[a]	7 (%)[a]
1	$BF_3 \cdot Et_2O$ (1.1)	0	CH_2Cl_2	0	28	50
2	H_2SO_4 (1.0)	50	THF	0	0	10
3	$KN(SiMe_3)_2$ (1.1)	0	THF	68	0	0

[a]Isolated yield.

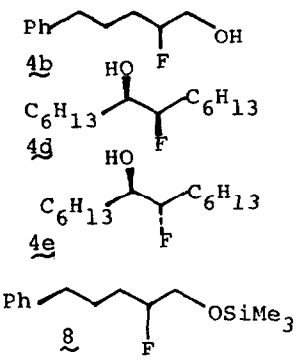


2d → 3d + 3e : KN(SiMe$_3$)$_2$ (1.1 eq), Et$_2$O, 0 °C, 63% (3d:3e = 45:55) (1)

2e → 72% (3d:3e = 2:98) (2)

Table 4. Desilylation of β-Fluoro-β-silyl Alcohols.

Entry	Substrate	Conditions[a]	Product	%yield[b]
1	2b	A	4b	70
2	2b	B	4b	67
3	2d	A	4d	89
4	2d	B	4d	78
5	2e	A	4e	73
6	2e	B	4e	56



[a]Conditions, A: n-Bu_4NF (1-2 eq) in THF at 0 °C
B: NaH (0.1 eq)/ 18-C-6 (0.1 eq) in THF at 0 °C--rt.
[b]Isolated yield.

The stereospecific desilylation of 2 was readily conducted with *n*-Bu_4NF in THF, and the fluorohydrins(4) were obtained in good yield with retention of configuration at the carbon bearing a fluorine (see Table 4). No rearrangement giving carbonyl compounds via carbenoid-like species was observed under these conditions. Another interesting desilylation was also observed in the presence of a catalytic amount of NaH/18-Crown-6 in THF, where the rearranged silyl

ether (8) as mixed with the fluorohydrin (4b) was obtained from 2b on rapid workup. 4b was most conveniently isolated after aqueous hydrolysis for complete desilylation. In these cases, the desilylation also proceeded with retention of configulation at the carbon bearing a fluorine.[10] This procedure enables us to synthesize 2-mono- or 1,2-dialkylsubstituted 2-fluoroethanols that were not affordable at all by the SiF_4 promoted ring opening-fluorination of mono- or 1,2-dialkylsubstituted oxiranes.[3]

References and Notes

(1) E. W. Colvin, "*Silicon in Organic Synthesis*", Butterworths, London, 1981, pp. 83-96 and references cited therein; *idem.*, "*Silicon Reagents in Organic Synthesis*", Academic Press, Galasgow, 1988, pp. 21-24.

(2) T. H. Chan, P. W. K. Lau, and M. P. Li, *Tetrahedron Lett.*, 2667, (1976).

(3) M. Shimizu and H. Yoshioka, *Tetrahedron Lett.*, 29, 4101 (1988).

(4) 2d and 2e exhibit the following spectra: 2d: ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9 H), 0.72-1.90 (m, 27 H, including an OH proton), 3.86 (dm, 1 H, J = 17.9 Hz); ^{19}F NMR ($CDCl_3/CFCl_3$) -187.1 ppm. 2e: ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9 H), 0.74-2.00 (m, 27 H, including an OH proton), 3.82 (dm, 1 H, J = 17.9 Hz); ^{19}F NMR ($CDCl_3/CFCl_3$) -188.0 ppm.

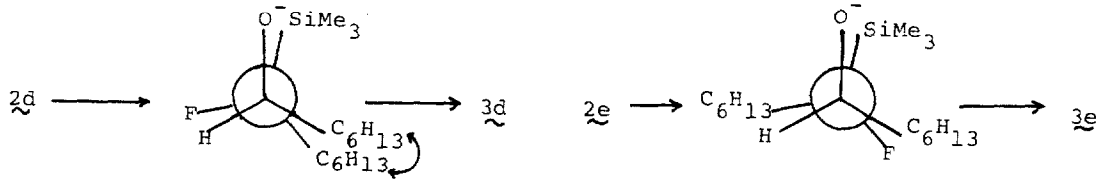
(5) D. J. Ager, *Synthesis*, 384 (1984) and references cited therein.

(6) P. F. Hudrlik, A. M. Hudrlik, R. J. Rona, R. N. Misra, and G. P. Withen, *J. Am. Chem. Soc.*, 99 1993 (1977).

(7) 3d and 3e exhibit the following spectra: 3d: ^{1}H NMR ($CDCl_3$) δ 0.75-1.64 (m, 22 H), 1.74-2.49 (m, 4 H), 4.99 (dt, 1 H, J = 21.5 and 7.6 Hz); ^{19}F NMR ($CDCl_3/CFCl_3$) -105.6 ppm. 3e: ^{1}H NMR ($CDCl_3$) δ 0.82-1.55 (m, 22 H), 1.88-2.36 (m, 4 H), 4.46 (dt, 1 H, J = 38.5 and 7.4 Hz); ^{19}F NMR ($CDCl_3/CFCl_3$) -110.6 ppm.

(8) There are only a few examples available for the stereoselective synthesis of fluoroalkenes: G. Boche and U. Fahrmann, *Chem. Ber.*, 114, 4005 (1981); S. H. Lee and J. Swartz, *J. Am. Chem. Soc.*, 108, 2445 (1986) and references cited therein.

(9) The intermediates alkoxides are shown below:



(10) 4d and 4e give the following spectra: 4d: ^{1}H NMR ($CDCl_3$) δ 0.68-1.72 (m, 27 H, including an OH proton), 3.57 (dm, 1 H, J = 18.2 Hz), 4.30 (dm, 1 H, J = 48.7 Hz); ^{19}F NMR ($CDCl_3/CFCl_3$) -195.5 ppm. 4e: ^{1}H NMR ($CDCl_3$) δ 0.74-1.92 (m, 27 H, including an OH proton), 2.70 (dm, 1 H, J = 17.7 Hz), 4.42 (dm, 1 H, J = 48.3 Hz); ^{19}F NMR ($CDCl_3/CFCl_3$) -191.4 ppm. These spectra are identical with those of the authentic samples prepared via the ring opening-fluorination of *cis*- and *trans*-1,2-dihexyloxiranes with Et_3N·3HF, respectively.

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