Bis(acylsilanes) and Trifluoromethyltrimethylsilane: A Useful System for the Synthesis of Cyclic 2,2-Difluoro-3-trialkylsilyl-1,3-ketols and Cyclic 2-Fluoro-1,3-diketones[1]

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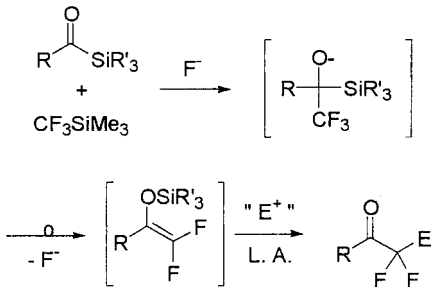
We report a one-pot reaction of bis(acylsilanes) with trifluoromethyltrimethylsilane (TFMTMS) leading to a new family of 2,2-difluoro-3-trialkylsilylketols **4**. These compounds were submitted to a facile and effective defluorosilylation. The overall process constitutes a new synthesis of cyclic six- and seven-membered 2-fluoro-1,3-diketones **8**, with regiospecific introduction of fluorine. The keto−enol equilibrium of cyclic 1,3-diketones and the mechanism of the defluorosilylation reaction were also studied.

Acylsilanes are interesting substrates[2] whose chemistry includes the properties of ketones and is enriched by specific properties, mainly due to their ability to undergo a silicon migration from carbon to oxygen (Brook rearrangement)[3] under nucleophilic addition. We have taken advantage of this rearrangement to synthesize new organofluorosilicon intermediates from acylsilanes and perfluoroorganometallic reagents and to develop several applications in organofluorine chemistry.[4,5,6] In addition to perfluoroalkyllithium and magnesium reagents,[4] trifluoromethyltrimethylsilane (TFMTMS)[7] has proven to be a convenient reagent giving access to a variety of *gem*-difluoro and fluoro derivatives.[5] Roughly, the key intermediate of this chemistry is a perfluoroenol (difluoroenol) silyl ether also called perfluoro (difluoro) enoxysilane (Scheme 1).

Scheme 1



In general, bis(acylsilanes) have been studied less than their monofunctionalized congeners, despite the potential contribution of intramolecular processes. After some synthesis and reactivity studies reported in the literature,[8] we undertook a more systematic investigation of these compounds.[9] Recently, we reported a preliminary account of the synthesis of 2,2-difluoro-3-trialkylsilyl ketols from acylsilanes and TFMTMS, via a difluoroenol silyl ether and its aldol reaction with an acylsilane.[6] We disclosed in this report the feasibility of the intramolecular counterpart from a 1,5-bis(acylsilane) and, on the other hand, of the conversion of the 2,2-difluoro-3-trialkylsilyl ketol into a 2-fluoro-1,3-diketone. We have since fully investigated the reaction of a variety of bis-

(1) Mixed Organofluorine-Organosilicon Chemistry, Part 15. Part 14: Lefebvre, O.; Brigaud, T.; Portella, C. *J. Org. Chem*., in press.

(2) For reviews, see: (a) Fleming, I. In *Comprehensive Organic Chemistry*; Jones, N., Ed.; Pergamon Press: Oxford, 1979; Vol. 3, Chapter 13, p 647. (b) Magnus, P. D.; Sarkar, T.; Djuric, S. In *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, 1982; Vol. 7, Chapter 48, p 631. (c) Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647. (d) Page, P. C. B.; Klair, S. S.; Rosenthal, S. *Chem. Soc. Rev.* **1990**, *19*, 147. (e) Cirillo, P. F.; Panek, J. S. *Org. Prep. Proced. Int.* **1992**, *24*, 555. (f) Najera, C.; Yus, M. *Org. Prep. Proced. Int.* **1995**, *27*, 400. (g) Qi, H.; Curran, D. P. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Moody, C. J., Eds.; Pergamon: Oxford, 1995; Chapter 5.09, p 409. (h) Bonini, B. F.; Comes-Franchini, M.; Fochi, M.; Mazzanti, G.; Ricci, A. *Gazz. Chim. Ital.* **1997**, *127*, 619. (i) Bonini, B. F.; Comes-Franchini, M.; Fochi, M.; Mazzanti, G.; Ricci, A. *J. Organomet. Chem.* **1998**, *567*, 181.

(3) (a) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77. (b) Brook, A. G.; Bassindale, A. R. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 2, Essay 9, p 149.

(4) Portella, C.; Dondy, B. *Tetrahedron Lett.* **1991**, *32*, 83. (b) Dondy, B.; Doussot, P.; Portella, C. *Synthesis* **1992**, 995. (c) Dondy, B.; Portella, C. *J. Org. Chem.* **1993**, *58*, 6671. (d) Doussot, P.; Portella, C. *J. Org. Chem.* **1993**, *58*, 6675.

(5) (a) Brigaud, T.; Doussot, P.; Portella, C. *J. Chem. Soc., Chem. Commun.* **1994**, 2117. (b) Brigaud, T.; Lefebvre, O.; Plantier-Royon, R.; Portella, C. *Tetrahedron Lett.* **1996**, *37*, 6115. (c) Lefebvre, O.; Brigaud, T.; Portella, C. *Tetrahedron* **1998**, *54*, 5939. (d) Lefebvre, O.; Brigaud, T.; Portella, C. *Tetrahedron* **1999**, *55*, 7233.

(6) Saleur, D.; Brigaud, T.; Bouillon, J.-P.; Portella, C. *Synlett* **1999**, 432.

(7) Reviews on the chemistry of TFMTMS: (a) Prakash, G. K. S.; Yudin, A. K. *Chem. Rev.* **1997**, *97*, 757. (b) Singh, R. P.; Shreeve, J. M. *Tetrahedron* **2000**, *56*, 7613.

(8) Mandai, T.; Yamaguchi, M.; Nakayama, Y.; Otera, J.; Kawada, M. *Tetrahedron Lett.* **1985**, *26*, 2675. (b) Capperucci, A.; Degl'Innocenti, A.; Faggi, C.; Ricci, A. *J. Org. Chem.* **1988**, *53*, 3612. (c) Chuang, T.-H.; Fang, J.-M.; Jiaang, W.-T.; Tsai, Y.-M. *J. Org. Chem.* **1996**, *61*, 1794. (d) Bonini, B. F.; Comes-Franchini, M.; Fochi, M.; Mazzanti, G.; Nanni, C.; Ricci, A. *Tetrahedron Lett.* **1998**, *39*, 6737.

(9) Bouillon, J.-P.; Portella, C. *Tetrahedron Lett.* **1997**, *38*, 6595. (b) Saleur, D.; Bouillon, J.-P.; Portella, C. *Tetrahedron Lett.* **1999**, *40*, 1885. (c) Bouillon, J.-P.; Portella, C. *Eur. J. Org. Chem.* **1999**, 1571. (d) Saleur, D.; Bouillon, J.-P.; Portella, C. *Tetrahedron Lett.* **2000**, *41*, 321. (e) Bouillon, J.-P.; Saleur, D.; Portella, C. *Synthesis* **2000**, 843. (f) Bouillon, J.-P.; Portella, C.; Bouquant, J.; Humbel, S. *J. Org. Chem.* **2000**, *65*, 5823.

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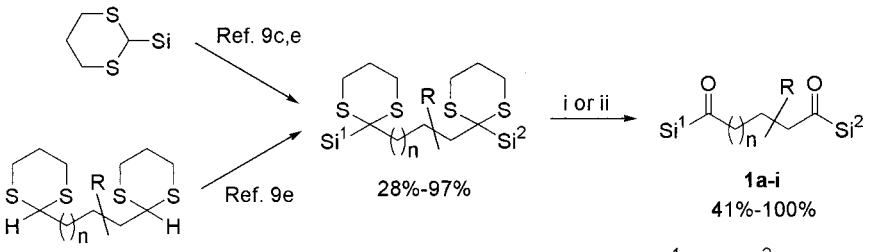
Table 1. Two-Step Synthesis of Aldols 4c−e,g

entry	*n*	bis(Ac)	conv (%)	mono(difluoroenoxysilane) (%)	bis(difluoroenoxysilane) (%)	aldol (%)
1	0	R = H: **1a**	100	**2a** (73)		
2	1	R = H: **1c**	76	**2c** (52)	**3c** (22)	**4c** (60)[a]
3	1	R = 2-Me: **1d**	89	R = 2-Me:**2d** (76)		R = 4-Me: **4d** (81)[a,b]
4	1	R = H: **1e**	100	**2e** (72)		**4e** (78)[a]
5	2	R = H: **1g**	64	**2g** (51)	**3g** (12)	**4g** (57)[c]

[a] $BiCl_3$ (0.4 equiv); conversion: 100%. [b] Mixture of diastereomers (58/42). [c] $BiCl_3$ (4.0 equiv).

Scheme 2



n	Si^1	Si^2	R	Cpd
0	TMS	TIPS	H	**1a**
1	TMS	TMS	H	**1b**
1	TBDMS	TBDMS	H	**1c**
1	TBDMS	TBDMS	2-Me	**1d**
1	TMS	TIPS	H	**1e**
1	TMS	TIPS	3-Ph	**1f**
2	TBDMS	TBDMS	H	**1g**
2	TBDMS	TBDMS	3-Ph	**1h**
2	TMS	TIPS	H	**1i**

Reagents: (i) $Hg(ClO_4)_2$, $CaCO_3$; (ii) I_2, $CaCO_3$

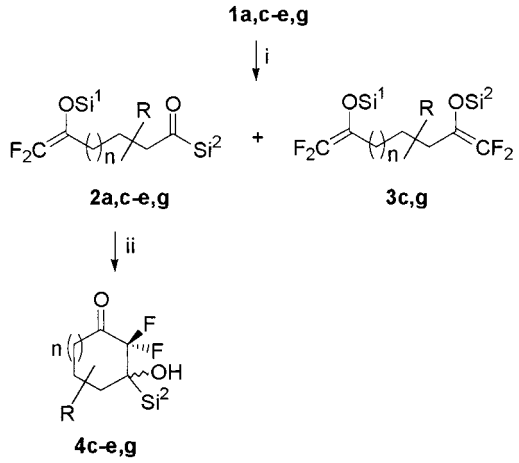
(acylsilanes) with TFMTMS, to assess the scope and limitations of this chemistry and of its application to elaborated cyclic 2-fluoro-1,3-diketones. This paper is a full account of this study, including some interesting observations on the keto−enol equilibrium of cyclic fluorodiketones.

Results and Discussion

The bis(acylsilanes) **1a**−**i** were prepared, in most cases with good overall yields, via the corresponding bis(dithianes) according to Scheme 2 and procedures already described.[9c,e]

The main problem to resolve was achieving a selective reaction of one acylsilane function with TFMTMS, to keep the second one available for the intramolecular aldol reaction. The results of the reaction of some representative bis(acylsilanes) with TFMTMS under fluoride activation (tetrabutylammonium difluorotriphenylstannate, DFTPS)[10,11] are depicted in Scheme 3 and Table 1. As one could expect, the symmetrical bis(acylsilanes) **1c,g** failed to give the mono(difluoroenol) silyl ethers **2c,g** with a high selectivity (Table 1, entries 2, 5), as a minor amount of the corresponding bis(difluoroenoxysilanes) **3c,g** was inevitably formed. We hypothesized that modification of the environment of one of the two carbonyl groups should favor a regioselective addition of the nucleophilic trifluoromethyl group. This could be possible by increasing the steric hindrance of substituents on

Scheme 3



Reagents: (i) CF_3TMS, DFTPS (cat.), CH_2Cl_2, -10°C; (ii) $BiCl_3$, rt

either of the two sides of one carbonyl function. Two types of nonsymmetrical bis(acylsilanes) have been designed for this purpose. Compound **1d** has an α position substituted by a methyl group. In compounds **1a,e**, the bulkiness of the trialkylsilyl groups are clearly differentiated (TMS and TIPS). The regioselectivity of the reaction is indeed highly enhanced with these nonsymmetrical substrates, since in each case a single regioisomer was observed (Table 1, entries 1, 3, 4). The structure **2d** was established unambiguously by an HMBC experiment which exhibits a ^2J coupling between the enol carbon and the two α-methylene protons and between the carbonyl carbon and the tertiary α′-proton. Compounds **2a,e** also result from a trifluoromethylation step on the less

(10) Previous study in this series (ref 5a) disclosed a self-condensation of the intermediate difluoroenoxysilane when using TBAF, whereas tetrabutylammonium difluorotriphenylstannate proved to be an excellent reagent for our purpose.

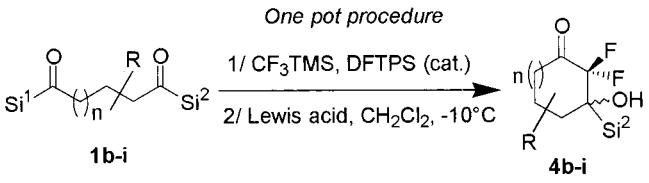
(11) (a) Gingras, M. *Tetrahedron Lett.* **1991**, *32*, 7381. (b) Kerverdo, S.; Fernandez, X.; Poulain, S.; Gingras, M. *Tetrahedron Lett.* **2000**, *41*, 5841.

Table 2. One-Pot Synthesis of Aldols 4b−i

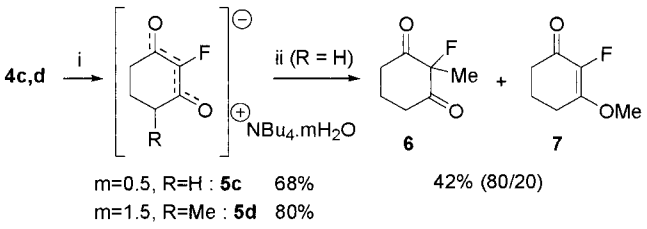
entry	*n*	Bis(Ac)	Si^1	Si^2	Lewis acid (equiv)	aldol (% yield)	byproducts (% yield)
1	1	R = H: **1b**	TMS	TMS	$Yb(OTf)_3$ (0.1)	**4b** (33)	(15)[d]
2	1	R = H: **1c**	TBDMS	TBDMS	$BiCl_3$ (0.4)	**4c** (35)	**3c** (20)
3	1	R = 2-Me: **1d**	TBDMS	TBDMS	$BiCl_3$ (1.0)	R = 4-Me: **4d** (52)[a]	
4	1	R = H:**1e**	TMS	TIPS	$BiCl_3$ (1.0)	**4e** (57)	
5	1	R = 3-Ph: **1f**	TMS	TIPS	$BiCl_3$ (0.4)	R = 5-Ph: **4f** (28)[b]	
6	2	R = H: **1g**	TBDMS	TBDMS	$BiCl_3$ (2.0)	**4 g** (41)	
7	2	R = 3-Ph: **1h**	TBDMS	TBDMS	$BiCl_3$ (2.0)	R = Ph: **4h** (45)[c]	
8	2	R = H: **1i**	TMS	TIPS	BF_3OEt_2 (1.4)	**4i** (36)	**8i** (8)

[a] Mixture of diastereomers (53/47). [b] Mixture of diastereomers (92/8). [c] Conversion: 83%; 2 regioisomers (5-Ph and 6-Ph), each as a mixture of diastereomers. [d] 2,6-Bis(trimethylsilyl)-4H-pyrane (see ref 9b,e).

Scheme 4

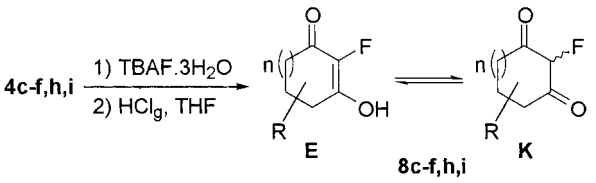


Scheme 5



Reagents: i: 1) TBAF.3H_2O, THF, 2) Recristallization; ii: MeI

Scheme 6



hindered TMS side since the TIPS group remains on the subsequent ketol **4e** (vide infra).

The isolated difluoroenoxysilanes **2** were then activated with a Lewis acid in order to induce a Mukaiyama type intramolecular aldol reaction (Scheme 3, Table 1). Bismuth trichloride[12] proved to be the best Lewis acid for this cyclization, which led to the C-trialkysilyl ketols **4**, except for the 1,4-derivative **2a**, which failed to give the corresponding five-membered ketol. Fair to good yields of six-membered (**4c**−**e**) as well as seven-membered (**4g**) cyclic silyl ketols were prepared in this way.

The second goal was to perform the overall transformation **1**→**4** in a one-pot process, the cyclization being induced by activation of the difluoroenol silyl ether prepared in situ. The results are collected in Scheme 4 and Table 2. The symmetrical bis(acylsilanes) **1b**,**c,g** gave the corresponding silyl difluoroaldols **4b,c,g** in rather poor yields after isolation from a multicomponent mixture, owing to the incomplete regioselectivity of the first step (entries 1, 2, 6). Nevertheless the overall yields are similar to those of the sequential process (Tables 1, 2). The reaction of the bis(TMS) derivative **1b** gave some 2,6-bis(trimethylsilyl)-4H-pyran as a cyclodehydration byproduct.[9b,e] Better results were obtained from nonsymmetrical bis(acylsilanes). Compounds **1d,e** were converted into the six-membered aldols **4d**,**e** with a good overall yield (Table 2, entries 3, 4). Taking into account that the intermediate difluoroenols **2d,e** are themselves the result of a multistep sequence, the overall conversion of bis(acylsilanes) **1d**,**e** into **4d,e** may be considered as a highly effective chemical process. The phenyl substituted 1,5-bis(acylsilane) **1f** led to the corresponding ketol **4f** in lower yield (Table 2, entry 5) owing to a more difficult aldol type cyclization. Finally, extension of this one-pot chemistry to the synthesis of seven-membered 2,2-difluoro-1,3-ketols worked, giving compounds **4h** and **4i** in fair overall yields (Table 2, entries 7, 8). It is worth noting that the reaction of **1i** with TFMTMS and $BiCl_3$ gave no aldol product **4i**. Nevertheless, the reaction using boron trifluoride as Lewis acid (Table 2, entry 8) produced the aldol **4i** in moderate yield (36%), accompanied by a small amount of the corresponding 2-fluoro-1,3-diketone (8%) (vide infra). Despite a good stability allowing their purification over silica gel, and an apparent high purity according to spectral analysis, we had difficulties in obtaining accurate microanalyses of most of the ketols **4**, this may be due to traces of hydration of the difluorocarbonyl moiety.

The structural characterization of ketols **4** was not problematic, although the substituted derivatives deserve some complementary comments. The two diastereomers of the methyl substituted ketol **4d** have been separated by silica gel flash chromatography. An X-ray analysis[13] of the minor isomer confirmed the position of the methyl group and showed its cis relationship with the TBDMS group. The ketol **4f** was obtained as a 92/8 mixture of compounds that seem to be diastereomers, although a full characterization of the minor component proved to be difficult. The case of the phenyl substituted compound **4h**, which gave an isomeric mixture of four compounds (66/22/8/4), is somewhat more complicated. Two regioisomers, each as a mixture of two diastereomers, were obtained. The isomeric nature of the four components of the isolated mixture was confirmed by chemical ionization GC-MS analysis. We have not attempted to assign the phenyl position owing to the suppression of this regiochemical issue in the subsequent step (see Scheme 6).

The ketols **4** seemed to be good candidates toward the preparation of cyclic 2-fluoro-1,3-diketones, which would

(12) (a) Le Roux, C.; Maraval, M.; Borredon, M. E.; Gaspard-Iloughmane, H.; Dubac, J. *Tetrahedron Lett.* **1992**, *33*, 1053. (b) Le Roux, C.; Gaspard-Iloughmane, H.; Dubac, J.; Jaud, J.; Vignaux, P. *J. Org. Chem.* **1993**, *58*, 1835. (c) Le Roux, C.; Gaspard-Iloughmane, H.; Dubac, J. *J. Org. Chem.* **1994**, *59*, 2238.

(13) The X-ray structure of the minor isomer of the aldol **4d** has been deposited at the Cambridge Crystallographic Data Center and allocated the deposition number CCDC113502.

Table 3. Synthesis of Cyclic 2-Fluoro-1,3-diketones 8c−f,h,i

entry	aldol	*n*	dicarbonyl compounds (%)	**E**/**K**[a]
1	**4c**	1	R = H: **8c** (68)[b]	95/5
2	**4d**	1	R = 6-Me: **8d** (80)	87/13[c]
3	**4e**	1	R = H: **8c** (74)	95/5
4	**4f**	1	R = 5-Ph: **8f** (92)	100/0
5	**4h**	2	R = 5-Ph: **8h** (70)	0/100[d]
6	**4i**	2	R = H: **8i** (56)	0/100

[a] By ^{19}F NMR in $CDCl_3$. [b] **8c** = **8e**, see ref 16a,b. [c] **8dK** is a 90/10 mixture of isomers, probably diastereomers according to a well-defined CHF group in the ^1H-, ^{19}F- and ^{13}C NMR spectra for the minor component. [d] Mixture of diastereomers (52/48).

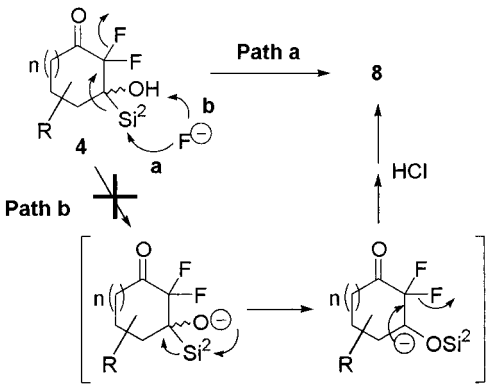
result from a thermodynamically favorable elimination of a fluorotrialkylsilane.[6] The α-fluorination of 1,3-diketones with electrophilic fluorination reagents is well documented. Xe−F[14] and O−F[15] bond based reagents and elemental fluorine[16] are not easy to handle and often are not completely selective for monofluorination. The N−F bond based reagents are the most effective for monofluorination.[17] All these fluorination methods start from the corresponding 1,3-diketone, and more particularly the cyclic diketone. A process which would associate the cyclization step with a regiospecific introduction of fluorine would constitute a complementary methodology for compounds derived from non commercially available or not easily prepared cyclic 1,3-diketones.

Treatment of the ketol **4** with tetrabutylammonium fluoride trihydrate in THF allowed an effective elimination of fluorotrialkylsilane. Instead of the expected 2-fluoro-1,3-diketone, crystallization from the crude reaction mixture led to the corresponding tetrabutylammonium salt (Scheme 5). The salt **5c** was isolated in good yield under optimized conditons (1 equiv of TBAF·$3H_2O$, crystallization from petroleum ether/AcOEt). The methyl substituted analogue **5d** was also isolated in good yield, however, application of the same conditions to the seven-membered ketol **4g** failed to give an isolated salt. The salts **5c** and **5d** crystallized with water, as indicated by elemental analysis and by the strong infrared absorption above 3300 cm^{-1}. The structure was corroborated by methylation. Treatment of **5c** with methyl iodide gave a mixture of C- and O-methyl derivatives **6** and **7** in a ratio 80/20 (Scheme 5).

The desired 2-fluorocyclohexan-1,3-diones **8c**−**f** were obtained in good yields after treatment of the reaction mixture by a THF solution of dry HCl (Scheme 6, Table 3). The dry workup avoided the drawbacks inherent to the easy hydration of this type of 1,3-diketone.[16b] This process worked with the α-substituted compound **4d**, with the more hindered TIPS derivatives **4e,f** and with the seven-membered ketols **4h,i** (Scheme 6, Table 3).

As already observed for 2-fluorocyclohexan-1,3-dione **8c**,[16a] the variously substituted 2-fluorocyclohexan-1,3-diones **8c**−**f** are in equilibrium with their enol tautomer, the equilibrium being in favor of the enol form **E** (Table 3). In contrast, the 2-fluorocycloheptan-1,3-diones **8h,i** are the only observable tautomer **K**, at least in the conditions of the NMR analysis. When an sp_2C-F/sp_3C-F bond is involved in a keto−enol or imino-enamino tautomeric equilibrium, the more favored tautomer, for acyclic compounds, is the one containing the sp_3C-F bond.[16a,18] Purrington et al. explained the exceptional behavior of 2-fluorocyclohexan-1,3-dione: fluorine destabilizes the enol, but this destabilizing effect is balanced in the rigid cyclic system by secondary orbital overlaps.[16a] The case of cycloheptan-1,3-dione is somewhat different: in addition to the electronic factor (destabilization of the enol due to sp_2C-F bond), one has to consider, as for nonfluorinated analogues,[19] an entropic contribution, due to the loss of flexibility when the diketone is converted into the enol.

Scheme 7



With regard to the defluorosilylation mechanism, two pathways may be considered with fluoride acting either as a nucleophile or as a base. The 2-fluoro-1,3-diketones **8** may result from an attack of the fluoride on silicon followed by a *β*-elimination of fluoride (Scheme 7, path a) or by deprotonation of the hydroxyl group followed by the Brook rearrangement-*β*-elimination sequence (Scheme 7, path b). Although the actual mechanism remains to be ascertained, the absence of reaction when the ketol **4c** is treated with another base such as sodium hydride favors the first alternative.

Conclusion

This work emphasizes the usefulness of the acylsilane functionality for the synthesis of elaborated organofluorine compounds. The extension to bis(acylsilanes) of the already well examplified one-pot reaction with TFMTMS leads to a new family of 2,2-difluoro-3-trialkylsilylketols

(14) XeF_2: (a) Zajc, B.; Zupan, M. *J. Chem. Soc., Chem. Commun.* **1980**, 759. (b) Tsushima, T.; Kawada, K.; Tsuji, T. *Tetrahedron Lett.* **1982**, *23*, 1165. (c) Zajc, B.; Zupan, M. *J. Org. Chem.* **1982**, *47*, 573. XeF_6C_{19}: (d) Yemul, S. S.; Kagan, H. B.; Setton, R. *Tetrahedron Lett.* **1980**, *21*, 277.

(15) Stavber, S.; Sket, B.; Zajc, B.; Zupan, M. *Tetrahedron* **1989**, *45*, 6003.

(16) (a) Purrington, S. T.; Bumgardner, C. L.; Lazaridis, N. V.; Singh, P. *J. Org. Chem.* **1987**, *52*, 4307. (b) Chambers, R. D.; Hutchinson, J.; Batsanov, A. S.; Lehmann, C. W.; Naumov, D. Y. *J. Chem. Soc., Perkin Trans. 1* **1996**, 2271. (c) Chambers, R. D.; Greenhall, M. P.; Hutchinson, J. *Tetrahedron* **1996**, *52*, 1.

(17) *N*-Fluoropyridinium: (a) Umemoto, T.; Fukami, S.; Tomizawa, G.; Harasawa, K.; Kawada, K.; Tomita, K. *J. Am. Chem. Soc.* **1990**, *112*, 8563. (b) Umemoto, T.; Nagayoshi, M.; Adachi, K.; Tomizawa, G. *J. Org. Chem.* **1998**, *63*, 3379. *N*-Fluorosulphonamide: (c) Xu, Z.-Q.; DesMarteau, D. D.; Gotoh, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 179. (d) Resnati, G.; DesMarteau, D. D. *J. Org. Chem.* **1991**, *56*, 4925. (e) Resnati, G.; DesMarteau, D. D. *J. Org. Chem.* **1992**, *57*, 4281. Selectfluor: (f) Banks, R. E.; Lawrence, N. J.; Popplewell, A. L. *J. Chem. Soc., Chem. Commun.* **1994**, 343.

(18) (a) Semmingsen, D. *Acta Chem. Scand., Ser. B.* **1974**, *28*, 169. (b) Tellier, F.; Sauvetre, R.; Normant, J.-F. *Tetrahedron Lett.* **1986**, *27*, 3147. (c) Bumgardner, C. L.; Whangbo, M.-H. In *Fluorine-Containing Molecules: Structure, Reactivity, Synthesis, and Applications*; Liebman, J. F., Greenberg, A., Dolbier, W. R., Jr., Eds; VCH: New York and Weinheim, 1988; Chapter 5, p 83. (d) Portella, C.; Iznaden, M. *Tetrahedron Lett.* **1988**, *29*, 3683. (e) Iznaden, M.; Portella, C. *J. Fluorine Chem.* **1989**, *43*, 105.

(19) Eistert, B.; Haupter, F.; Schank, K. *Liebigs Ann. Chem.* **1963**, *665*, 55.

4. These compounds can be subjected to a facile and effective defluorosilylation. The overall process constitutes a total synthesis of cyclic 6- and 7-membered 2-fluoro-1,3-diketones **8**, with the regiospecific introduction of fluorine being concomitant with the ring construction. Such a method may be of interest, in addition to the direct fluorination of 1,3-diketones by electrophilic fluorination reagents, for the synthesis of elaborated substituted derivatives.

Experimental Section

General methods are described in ref 20. CF_3TMS was provided by Bayer company (Leverkusen). $Bu_4N^+Ph_3SnF_2^-$ was prepared according to a reported procedure.[11]

General Two-Step Procedure, via Difluoroenoxysilanes 2. To a solution of the bis(acylsilane) **1** (4.56 mmol, 1.00 equiv) in CH_2Cl_2 (15 mL) at −10 °C were added trifluoromethyltrimethylsilane (CF_3SiMe_3) (5.74 mmol, 1.26 equiv) and then tetrabutylammonium difluorotriphenylstannate (DFTPS) (0.02 mmol, 0.05 equiv). After stirring for 1 h at room temperature, the mixture was hydrolyzed with water (20 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel using petroleum ether/diethyl ether (97/3) to give the mono(difluoroenoxysilane) **2a,c−e,g** and the bis(difluoroenoxysilane) **3c,g** (Table 1). To a solution of mono(difluoroenoxysilane) **2c−e,g** (1.00 mmol, 1.00 equiv) in CH_2Cl_2 (3 mL) was added $BiCl_3$ (0.4 or 4.0 equiv, see Table 1) at room temperature. After stirring for 1 day at room temperature, the mixture was filtered through Celite, then hydrolyzed with an aqueous solution of $NaHCO_3$ (15 mL). The aqueous phase was extracted with CH_2Cl_2 (4 × 10 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel using petroleum ether/AcOEt (90/10) to give the desired 2,2-difluoro aldol **4c−e,g** (Table 1). The aldols are described in the next section.

1-(*tert*-Butyldimethylsilyl)-5-(*tert*-butyldimethylsilyloxy)-6,6-difluoro-hex-5-en-1-one (2c). Oil; ^{1}H NMR δ 0.12 (s, 3H), 0.13 (s, 3H), 0.18 (s, 6H), 0.93 (s, 18H), 1.72 (tt, 2H, J_{HH} = 7.2, J_{HH} = 6.9), 2.0−2.1 (m, 2H), 2.61 (t, 2H, J_{HH} = 7.2); ^{13}C NMR δ −7.0, −4.8, 18.0, 18.2, 18.7, 25.5, 26.4, 28.0, 48.7, CF_2CO unvisible, 129.4 (dd, J_{CF} = 281.7, J_{CF} = 274.5), 246.7; ^{19}F NMR δ −106.2 (d, 1F, J_{AB} = 87.7), −120.9 (d, 1F, J_{AB} = 87.7); IR (film) 1755, 1647 cm^{-1}.

1-(*tert*-Butyldimethylsilyl)-5-(*tert*-butyldimethylsilyloxy)-6,6-difluoro-2-methyl-hex-5-en-1-one (2d). Oil; ^{1}H NMR δ 0.11 (s, 6H), 0.17 (s, 3H), 0.19 (s, 3H), 0.91 (s, 18H), 0.93 (d, 3H, J_{HH} = 8.8), 1.1−1.3 (m, 1H), 1.8−1.9 (m, 1H), 2.0−2.1 (m, 2H), 2.94 (m, 1H); ^{13}C NMR δ −6.53, −6.46, −4.8, 13.9, 16.7, 17.9, 25.4, 26.5, 26.6, 26.8, 49.4, 112.7 (dd, J_{CF} = 42.0, J_{CF} = 14.1), 153.5 (dd, J_{CF} = 282.6, J_{CF} = 275.7), 249.8; ^{19}F NMR δ −106.2 (d, 1F, J_{AB} = 87.7), −120.8 (d, 1F, J_{AB} = 87.7); IR (film) 1763, 1640 cm^{-1}.

1-(Tris-isopropylsilyl)-5-(trimethylsilyloxy)-6,6-difluoro-hex-5-en-1-one (2e). Oil; ^{1}H NMR δ 0.17 (s, 9H), 1.08 (d, 18H, J_{HH} = 7.2), 1.25 (sept, 3H, J_{HH} = 7.3), 1.70 (tt, 2H, J_{HH} = 7.3, J_{HH} = 6.9), 2.0−2.1 (m, 2H), 2.58 (t, 2H, J_{HH} = 7.3); ^{13}C NMR δ 0.03, 10.7, 17.9, 18.5, 28.0, 50.0, 112.8, 153.6 (dd, J_{CF} = 281.7, J_{CF} = 274.5), 246.6; ^{19}F NMR δ −106.5 (d, 1F, J_{AB} = 83.9), −121.2 (d, 1F, J_{AB} = 83.9); IR (film) 1763, 1640 cm^{-1}. Anal. Calcd for $C_{18}H_{36}F_2O_2Si_2$: C, 57.09; H, 9.58. Found: C, 56.88; H, 9.57.

2,6-Bis(*tert*-butyldimethylsilyloxy)-1,1,7,7-tetrafluoro-hept-1,6-ene (3c). Oil; ^{1}H NMR δ 0.14 (s, 12H), 0.94 (s, 18H), 1.72 (quint, 2H, J_{HH} = 7.2), 2.0−2.1 (m, 4H); ^{13}C NMR δ −4.9, 18.0, 22.4, 25.5, 28.0, 112.4 (dd, J_{CF} = 42.2, J_{CF} = 14.1), 153.6 (dd, J_{CF} = 281.7, J_{CF} = 274.6); ^{19}F NMR δ −106.3 (d, 2F, J_{AB} = 84.0), −121.0 (d, 2F, J_{AB} = 84.0); IR (film) 1772 cm^{-1}.

2,2-Difluoro Aldols 4; General One-Pot Procedure. To a solution of bis(acylsilane) **1b−i** (10.0 mmol, 1.00 equiv) in CH_2Cl_2 (30 mL) at −10 °C were added trifluoromethyltrimethylsilane (CF_3SiMe_3) (13.0 mmol, 1.30 equiv) then tetrabutylammonium difluorotriphenylstannate (DFTPS) (0.5 mmol, 0.05 equiv). The mixture was stirred for 30 min at room temperature. Lewis acid (0.1−2.0 equiv, see Table 2) was then added. After 1 day of stirring at room temperature, the mixture was filtered through Celite then hydrolyzed with an aqueous solution of $NaHCO_3$ (100 mL). The aqueous phase was extracted with CH_2Cl_2 (4 × 50 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel using petroleum ether/AcOEt (90/10) to give the desired 2,2-difluoro aldol **4b−i** (Table 2).

2,2-Difluoro-3-hydroxy-3-(*tert*-butyldimethylsilyl)-cyclohexanone (4c). Oil; ^{1}H NMR δ 0.15 (s, 6H), 1.01 (s, 9H), 1.75 (brs, 1H), 1.8−2.0 (m, 1H), 2.1−2.3 (m, 3H), 2.5−2.7 (m, 2H); ^{13}C NMR δ −6.6, −6.5, 18.1, 20.6, 27.3, 31.0 (d, J_{CF} = 7.9), 38.6, 75.2 (t, J_{CF} = 33.5), 117.1 (dd, J_{CF} = 259.9, J_{CF} = 252.0), 199.5 (t, J_{CF} = 27.6); ^{19}F NMR δ −106.6 (d, 1F, J_{AB} = 257.5), −123.2 (d, 1F, J_{AB} = 257.5); IR (film) 3470, 1752 cm^{-1}; MS (CI, NH_3) *m/e* (%) 282 (M + 1 + 17), 132 (100).

2,2-Difluoro-3-hydroxy-3-(*tert*-butyldimethylsilyl)-4-methyl-cyclohexanone (4d). Major Diastereomer. White solid: mp 80−82 °C; ^{1}H NMR δ 0.19 (s, 6H), 1.02 (s, 9H), 1.12 (d, 3H, J_{HH} = 6.9), 1.68 (brs, 1H), 1.7−1.8 (m, 1H), 2.03 (m, 1H), 2.4−2.5 (m, 2H), 2.70 (m, 1H); ^{13}C NMR δ −4.1, −3.9, 17.3, 18.8, 27.6, 29.6, 36.3 (d, J_{CF} = 4.2), 37.1, 75−76, 116.5 (dd, J_{CF} = 258.9, J_{CF} = 250.5), 199.5 (t, J_{CF} = 29.5); ^{19}F NMR δ −107.2 (d, 1F, J_{AB} = 255.6), −118.5 (d, 1F, J_{AB} = 255.6); IR (KBr) 3368, 1755 cm^{-1}; MS (CI, NH_3) *m/e* (%) 297 (M + 1 + 17), 260 (100), 211.

Minor Diastereomer. Oil; ^{1}H NMR δ 0.22 (d, 3H, J_{HF} = 1.9), 0.27 (d, 3H, J_{HF} = 1.2), 1.02 (s, 9H), 1.33 (dd, 3H, J_{HH} = 7.6, J_{HF} = 3.8), 1.6−1.7 (m, 1H), 1.82 (brs, 1H), 2.4−2.5 (m, 2H), 2.5−2.6 (m, 1H), 2.8−3.0 (m, 1H); ^{13}C NMR δ −5.2, 15.9 (d, J_{CF} = 8.4), 18.5, 27.9, 28.1, 34.5, 36.1 (d, J_{CF} = 8.4), 78.3 (dd, J_{CF} = 30.5, J_{CF} = 28.4), 117.2 (dd, J_{CF} = 257.8, J_{CF} = 253.6), 199.2 (dd, J_{CF} = 27.4, J_{CF} = 25.3 Hz); ^{19}F NMR δ −103.5 (d, 1F, J_{AB} = 263.2), −117.3 (d, 1F, J_{AB} = 263.2).

2,2-Difluoro-3-hydroxy-3-(*tris*-isopropylsilyl)-cyclohexanone (4e). White solid: mp 62−64 °C; ^{1}H NMR δ 1.17 (d, 18H, J_{HH} = 6.9), 1.31 (sept, 3H, J_{HH} = 6.9), 1.79 (brs, 1H), 1.8−1.9 (m, 1H), 2.1−2.3 (m, 3H), 2.5−2.7 (m, 2H); ^{13}C NMR δ 11.4, 19.1, 19.3, 20.4, 31.9 (d, J_{CF} = 9.9), 38.5, 76−78 (C_4), 116.7 (dd, J_{CF} = 260.6, J_{CF} = 248.9), 199.8 (dd, J_{CF} = 28.2, J_{CF} = 25.8); ^{19}F NMR δ −105.9 (d, 1F, J_{AB} = 251.8), −122.6 (d, 1F, J_{AB} = 251.8); IR (KBr) 3474, 1750 cm^{-1}; MS (CI, NH_3) *m/e* (%) 324 (M + 1 + 17), 287, 271 (100), 132. Anal. Calcd for $C_{15}H_{28}F_2O_2Si$: C, 58.79; H, 9.21. Found: C, 58.54; H, 9.23.

2,2-Difluoro-3-hydroxy-3-(*tert*-butyldimethylsilyl)-cycloheptanone (4 g). White solid: mp 53−55 °C; ^{1}H NMR δ 0.12 (s, 3H), 0.16 (s, 3H), 1.00 (s, 9H), 1.5−2.2 (m, 7H), 2.4−2.7 (m, 2H); ^{13}C NMR δ −6.4, −6.1, 18.3, 20.9, 21.8, 27.6, 33.5 (d, J_{CF} = 9.8), 38.6, 71.6 (dd, J_{CF} = 35.4, J_{CF} = 32.5), 121.3 (dd, J_{CF} = 255.0, J_{CF} = 252.0), 200.8 (dd, J_{CF} = 31.5, J_{CF} = 25.6); ^{19}F NMR δ −104.8 (d, 1F, J_{AB} = 251.8), −108.2 (d, 1F, J_{AB} = 251.8); IR (film) 3507, 1736 cm^{-1}; MS *m/e* (%) 278 (M^+), 261, 127 (100).

2,2-Difluoro-3-hydroxy-3-(*tert*-butyldimethylsilyl)-5 (or 6) -phenyl-cycloheptanone (4h). Oil. Isomeric mixture of four compounds (66/22/8/4). IR (film): 3517, 1738, 1466 cm^{-1}. HRMS: calcd. for $C_{19}H_{28}F_2O_2Si$ *m/e* = 354.1827; found 354.1832.

First Isomer (66%). ^{1}H NMR (500 MHz) δ 0.18 (m, 6H), 1.00 (s, 9H), 1.81 (brs, 1H), 2.0−2.2 (m, 3H), 2.6−3.1 (m, 4H), 7.2−7.3 (m, 5H); ^{13}C NMR (125 MHz) δ −6.41, −6.0, 18.4, 27.6, 29.4, 38.4, 38.5, 41.6 (d, J_{CF} = 9.8), 72.3 (dd, J_{CF} = 36.7, J_{CF} = 32.5), 121.0 (t, J_{CF} = 253.3), 126.3, 126.5, 128.7, 147.5, 200.2 (t, J_{CF} = 30.8); ^{19}F NMR δ −105.2 (d, 1F, J_{AB} = 251.7), −107.6 (d, 1F, J_{AB} = 251.7); GCMS (CI, NH_3, retention time: 9.31) *m/e* (%) 372 (M + 1 + 17), 335 (M + 1), 132, 52 (100).

(20) Bouillon, J.-P.; Didier, B.; Dondy, B.; Doussot, P.; Plantier-Royon, R.; Portella, C. *Eur. J. Org. Chem.* **2001**, 187.

Second Isomer (22%). Selected data: ^{1}H NMR (500 MHz) δ 0.14 (m, 6H), 0.99 (s, 9H); ^{13}C NMR (125 MHz) δ −6.37, 18.5, 31.2, 39.4, 43.8 (d, J_{CF} = 8.5), 72.4 (t, J_{CF} = 33.4), 121.2 (t, J_{CF} = 253.3), 128.8, 147.4; ^{19}F NMR δ −103.9 (d, 1F, J_{AB} = 247.9), −106.6 (d, 1F, J_{AB} = 247.9); GCMS (CI, NH_3, retention time: 10.13) *m/e* (%) 372 (M + 1 + 17), 335 (M + 1), 52 (100).

Third Isomer (8%). Selected data: ^{1}H NMR (500 MHz) δ 0.21 (m, 6H), 1.05 (s, 9H); ^{13}C NMR (125 MHz) δ 29.2, 41.8 (d, J_{CF} = 3.5); ^{19}F NMR δ −104.6 (d, 1F, J_{AB} = 251.7), −108.8 (d, 1F, J_{AB} = 251.7); GCMS (CI, NH_3, retention time: 9.36) *m/e* (%) 372 (M + 1 + 17), 335 (M + 1), 132, 52 (100).

Fourth Isomer (4%). Selected data: ^{1}H NMR (500 MHz) δ 1.04 (s, 9H); ^{13}C NMR (125 MHz) δ 29.7, 40.9 (d, J_{CF} = 3.4); ^{19}F NMR δ −105.8 (d, 1F, J_{AB} = 247.9), −110.3 (d, 1F, J_{AB} = 247.9); GCMS (CI, NH_3, retention time: 9.92) *m/e* (%) 372 (M + 1 + 17), 335 (M + 1), 52 (100).

Tetrabutylammonium Salts 5c,d; General Procedure. To a solution of 2,2-difluoro aldol **4c,d** (2.60 mmol, 1.00 equiv) in THF (60 mL) was added solid tetrabutylammonium fluoride trihydrate (TBAF·3H_2O, 3.20 mmol, 1.20 equiv). After stirring for 3 h at room temperature, the solvent was removed in vacuo. The residue was crystallized from a mixture of petroleum ether/AcOEt to give the tetrabutylammonium salt **5c,d**. These salts crystallized with water.

Tetrabutylammonium 2-Fluoro-cyclohexan-1,3-dionate (5c). Brown solid; ^{1}H NMR δ 1.00 (t, 12H, J_{HH} = 7.3), 1.43 (m, 8H), 1.6−1.7 (m, 8H), 1.85 (quint, 2H, J_{HH} = 6.1), 2.4−2.5 (m, 4H), 3.26 (m, 8H); ^{13}C NMR δ 13.5, 19.6, 20.9, 23.7, 35.0, 58.6, 142.6 (d, J_{CF} = 220.5), 179.4; ^{19}F NMR δ −176.5 (s); IR (KBr) 3422, 1609, 1512 cm^{-1}. Anal. Calcd for $C_{22}H_{42}FNO_2$ + 0.5 H_2O: C, 69.43; H, 11.39; N, 3.68. Found: C, 69.34; H, 11.68; N, 3.97.

Tetrabutylammonium 2-Fluoro-4-methyl-cyclohexan-1,3-dionate (5d). Brown solid; ^{1}H NMR δ 0.99 (t, 12H, J_{HH} = 7.3), 1.19 (d, 3H, J_{HH} = 6.9), 1.42 (m, 8H), 1.5−1.7 (m, 8H), 1.9−2.0 (m, 1H), 2.3−2.6 (m, 4H), 3.25 (m, 8H); ^{13}C NMR δ 13.3, 16.5, 19.4, 23.6, 28.5, 32.4, 38.8, 58.3, 142.4 (d, J_{CF} = 218.5), 176.5, 184.2; ^{19}F NMR δ −175.9 (s); IR (KBr) 3374, 1605, 1512 cm^{-1}. Anal. Calcd for $C_{23}H_{44}FNO_2$ + 1.5 H_2O: C, 66.95; H, 11.48; N, 3.39. Found: C, 66.57; H, 11.55; N, 3.08.

Alkylation of Tetrabutylammonium Salt 5c. To a solution of tetrabutylammonium salt **5c** (0.50 g, 1.35 mmol) in CH_2Cl_2 (10 mL) was added methyl iodide (0.38 g, 2.69 mmol). After stirring for 3 h at room temperature, the volatiles were removed in vacuo. The crude mixture was distilled under reduced pressure (T = 80 °C, P = 5 × 10^{-2} mbar) using a Kugelhor apparatus to give a mixture (42%) of C- and O-methyl derivatives **6** and **7** in a ratio 80/20.

2-Fluoro-2-methyl-cyclohexan-1,3-dione (6). ^{1}H NMR δ 1.70 (d, 3H, J_{HF} = 22.1), 1.8−2.0 (m, 2H), 2.7−2.9 (m, 4H); ^{13}C NMR δ 18.0, 20.3, 59.2, 101.0 (d, J_{CF} = 196.0), 202.0; ^{19}F NMR δ -161.6 (q, 1F, J_{HF} = 22.1).

2-Fluoro-3-methoxy-cyclohex-2-en-1-one (7). ^{1}H NMR δ 2.4−2.6 (m, 1H), 2.7−2.9 (m, 3H), 4.03 (d, 3H, J_{HF} = 4.6); selected ^{13}C NMR data: δ 20.0, 37.6, 59.1, 201.7; ^{19}F NMR δ −164.1 (s).

2-Fluoro-1,3-diketones 8; General Procedure. To a solution of 2,2-difluoro aldol **4** (5.00 mmol, 1.00 equiv) in THF (50 mL) was added solid tetrabutylammonium fluoride trihydrate (5.00 mmol, 1.00 equiv). After stirring for 2 days at room temperature, a saturated solution of HCl_g in THF (100 mL) was added. After stirring for 4 h at room temperature, the solvent was removed in vacuo. The crude mixture was chromatographed over silica gel using AcOEt as eluent. The 2-fluoro-1,3-diketones **8** were generally obtained as a mixture of tautomers **E/K** (see Table 3).

2-Fluoro-3-hydroxy-6-methyl-cyclohex-2-en-1-one (8dE). Oil; ^{1}H NMR δ 1.20 (d, 3H, J_{HH} = 6.9), 1.6−1.7 (m, 1H), 2.0−2.1 (m, 1H), 2.5−2.6 (m, 3H), 7.0−7.5 (m, 1H); ^{13}C NMR δ 15.7, 27.8, 29.5, 37.1, 139.8 (d, J_{CF} = 235.5), 171.9, 181.7; ^{19}F NMR δ −168.0 (s); IR (KBr) 3280, 1727, 1674, 1622 cm^{-1}; GCMS *m/e* (%) 144 (M$^+$), 102 (100), 55.

2-Fluoro-4-methyl-cyclohex-1,3-dione (8dK). Mixture of diastereomers (90/10).

Major Diastereomer. ^{1}H NMR δ 1.25 (d, 3H, J_{HH} = 7.2), 1.3−1.4 (m, 1H), 2.1−2.2 (m, 1H), 2.7−2.8 (m, 3H), 5.67 (d, 1H, J_{HF} = 46.7); ^{13}C NMR δ 13.1, 26.4, 38.2, 43.1, 98.1 (d, J_{CF} = 208.1), 198.2 (d, J_{CF} = 14.6), 199.3 (d, J_{CF} = 13.6); ^{19}F NMR δ −207.6 (d, J_{HF} = 45.8).

Minor Diastereomer. Selected data: ^{1}H NMR δ 5.88 (d, 1H, J_{HF} = 46.7); ^{13}C NMR δ 97.4 (d, J_{CF} = 208.1); ^{19}F NMR δ −212.7 (d, J_{HF} = 45.8).

2-Fluoro-3-hydroxy-5-phenyl-cyclohex-2-en-1-one (8fE). Oil; ^{1}H NMR δ 2.5−2.7 (m, 2H), 2.8−3.0 (m, 2H), 3.3−3.5 (m, 1H), 7.2−7.4 (m, 5H); ^{13}C NMR (CD_3COCD_3) δ 30.1, 40.4, 65.8, 127.4, 127.5, 129.2, 140.6 (d, J_{CF} = 236.0), 143.8, 167.1, 173.0; ^{19}F NMR δ −168.9 (s); MS *m/e* (%) 206 (M$^+$), 131, 104 (100). HRMS: calcd. for $C_{12}H_{11}FO_2$ *m/e* = 206.0740; found 206.0745.

2-Fluoro-5-phenyl-cycloheptan-1,3-dione (8hK). Mixture of diastereomers (52/48). White solid; IR (KBr) 1740, 1717, 1495 cm^{-1}; MS *m/e* (%) 220 (M$^+$), 200, 117 (100). HRMS: calcd. for $C_{13}H_{13}FO_2$ *m/e* = 220.0900; found 220.0908.

Major Diastereomer. ^{1}H NMR δ 2.1−2.5 (m, 2H), 2.6−3.1 (m, 5H), 5.84 (d, 1H, J_{HF} = 49.2), 7.1−7.4 (m, 5H); ^{13}C NMR δ 30.7, 39.8, 42.4, 49.9, 97.6 (d, J_{CF} = 198.8), 126.2, 127.2, 129.0, 144.5, 197.8 (d, J_{CF} = 16.7), 198.5 (d, J_{CF} = 16.7); ^{19}F NMR δ −194.6 (d, J_{HF} = 49.6).

Minor Diastereomer. Selected data: ^{1}H NMR δ 5.73 (d, 1H, J_{HF} = 49.2); ^{13}C NMR δ 31.5, 41.0, 41.7, 47.9, 97.8 (d, J_{CF} = 199.8), 126.3, 127.2, 129.0, 144.3, 198.5 (d, J_{CF} = 16.7), 198.8 (d, J_{CF} = 16.7); ^{19}F NMR δ −192.9 (d, J_{HF} = 45.8).

2-Fluoro-cycloheptan-1,3-dione (8iK). Oil; ^{1}H NMR δ 1.8−2.2 (m, 4H), 2.5−2.8 (m, 4H), 5.79 (d, 1H, J_{HF} = 48.8); ^{13}C NMR δ 23.1, 41.3, 97.7 (d, J_{CF} = 198.8), 199.0 (d, J_{CF} = 16.7); ^{19}F NMR δ −195.1 (d, J_{HF} = 49.6); IR (KBr) 1742, 1713 cm^{-1}; MS *m/e* (%) 144 (M$^+$), 116, 55 (100). HRMS: calcd. for $C_7H_9FO_2$ *m/e* = 144.0587; found 144.0585.

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Supporting Information Available: General procedures for the preparation of bis(acylsilanes) **1a**−**i** and their spectral data; spectral data of compounds **2a,g**, **3g**, **4b,f,i**. This material is available free of charge via the Internet at http://pubs.acs.org.

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