Mixed Organofluorine–Organosilicon Chemistry. 4. Perfluoroenoxysilanes: Synthesis and Reactivity

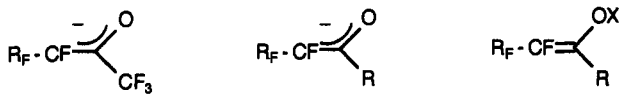
Pascale Doussot and Charles Portella*

Laboratoire des Réarrangements Thermiques et Photochimiques, associé au CNRS (URA no. 459), Faculté des Sciences, B.P. 347, F-51062 Reims Cédex, France

Received April 12, 1993•

1-Alkyl (or aryl)-1-[(trialkylsilyl)oxy]perfluoroalk-1-enes were synthesized from acylsilanes and perfluoroalkyl iodides. Perfluoroorganolithium and magnesium were used for aliphatic and aromatic derivatives, respectively. These enoxysilanes have nucleophilic as well as electrophilic properties. They are enolate equivalents, leading to 2-hydroperfluoroalkyl ketones on hydrolysis, or aldol products. With good nucleophiles like amines, they react as electron poor alkenes to give β-enamino ketones.

Fluorinated enolates have attracted increasing attention for some years.[1] The major difficulty encountered in the preparation and/or the reactions of β-fluoroenolates is to avoid the β-elimination of fluoride.[2] To overcome this problem, an alternative approach consists in the use of enolate equivalents prepared by a route that does not involve the enolate itself. Although perfluoroenolates **1** have been extensively studied,[3] to our knowledge in the type **2** enolate series only the parent enol phosphates **3** [X = $OPO(OEt)_2$][4] derived from perfluoroalkyl ketones, and aluminum enolates **3** [X = AlR_2][5] have been described.

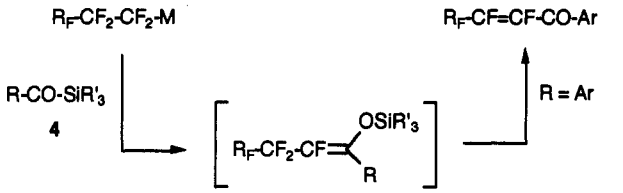


1 **2** **3**

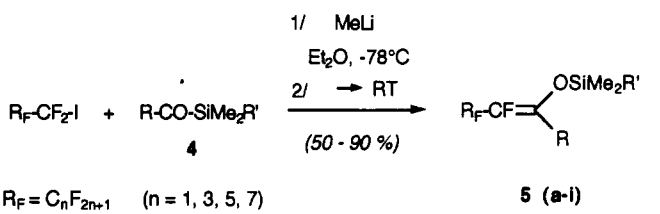
The fluorine substitution greatly modifies the electron distribution of these intermediates[6] which exhibit a wide spectrum of reactions. Perfluoroenolates **1** show both normal nucleophilic (i.e. aldol reaction with R_F = F) and electrophilic behavior (i.e. toward organometallic reagents).[3] Enol phosphates react with nucleophiles via the enones,[4] but they have to be transformed into aluminum enolates to exhibit aldol reactivity.[5]

We have previously reported the occurrence of the enoxysilanes **5** as intermediates in the reactions of acylsilanes **4** with perfluoroorganometallics,[7,8] leading in particular to the perfluoroalkenyl ketones[8] (Scheme I). The possibility to stop the reaction at the enoxysilane level would extend the scope of the reaction. We have found conditions to achieve this goal and we report in this paper the synthesis of various perfluoroenoxysilanes[9] **5**

Scheme I



Scheme II



($R_F = C_nF_{2n+1}$ (n = 1, 3, 5, 7); R = Alkyl, alk-1-enyl; R' = Me, t-Bu)

($R_F = C_nF_{2n+1}$; R = alkyl, aryl; R′ = alkyl) as well as their use in some representative applications.

Synthesis of Perfluoroenoxysilanes 5. Treatment of a mixture of aliphatic acylsilane and perfluoroalkyl iodide in ether with methyllithium at −78 °C,[10] followed by warming to room temperature, gave quantitatively the corresponding enoxysilane **5** (R = alkyl) after chromatographic and NMR analysis. Trimethylsilyl (TMS) derivatives **5a–c**, easily hydrolyzed, are difficult to isolate without contamination with the corresponding α-hydroperfluoroalkyl ketone. In contrast, *tert*-butyldimethylsilyl (TBDMS) analogues **5d–f** are much more stable and could be isolated as pure compounds in good yields (Scheme II and Table I). Within the limits of 300-MHz NMR and capillary GLC resolution, the reaction gave a single diastereomer whose configuration has not been clearly established.

The conjugated products **5g–i** were easily synthesized following the same procedure: the rearrangement was in these cases very fast and the enoxysilanes were formed without needing to keep the mixture at room temperature.

Perfluoroorganolithiums were not suitable for the synthesis of aromatic analogues of **5** (R = aryl). It has been previously shown that a fast reaction led directly to

• Abstract published in *Advance ACS Abstracts*, October 1, 1993.

(1) Ishihara, T. *Yuki Gasei Kagaku Kyskaishi* **1992**, *50*, 347.

(2) Recently, an "electrophile coexisting procedure" was proposed to quench the enolate before elimination of the β-fluoride: Qian, C.-P.; Nakai T. *Tetrahedron Lett.* **1990**, *31*, 7043.

(3) Qian, C-P.; Nakai, T. *Selective Fluorination in Organic and Bioorganic Chemistry*; Welch, J. T., Ed., ACS Symposium Series 456; American Chemical Society: 1991; p 18.

(4) Ishihara, T.; Okada, Y.; Kuroboshi, M.; Shinozaki, T.; Ando, T. *Chem. Lett.* **1988**, 819.

(5) Ishihara, T.; Kuroboshi, M.; Yamaguchi, K.; Okada, Y. *J. Org. Chem.* **1990**, *55*, 3107.

(6) Qian, C-P.; Nakai, T.; Dixon, D. A.; Smart, B. E. *J. Am. Chem. Soc.* **1990**, *112*, 4602.

(7) Dondy, B.; Portella, C. *Tetrahedron Lett.* **1991**, *32*, 83.

(8) Dondy, B.; Portella, C. *J. Org. Chem.*, preceding paper, in this issue.

(9) Although the nonfunctional part of the molecule is hydrogenated, we use the names perfluoroenolates and perfluoroenoxysilanes for **3** or **5**, respectively, for simplification reasons.

(10) For a review on perfluoroorganometallic reagents, see: Burton, D. J.; Yang, Z-Y. *Tetrahedron* **1992**, *48*, 189.

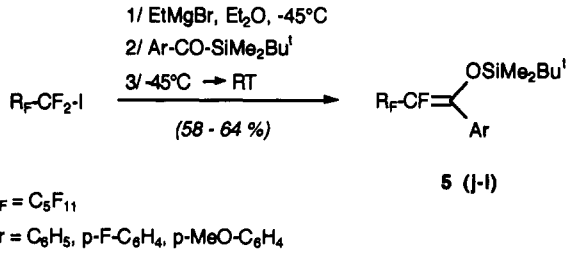
0022-3263/93/1958-6675$04.00/0

Table I. Enoxysilanes R_F-CF=C(OSiMe$_2$R')R Prepared

starting acylsilane	product	R	R'	R_F	method[a]	yield (%)[b]
4a	**5a**	n-C_5H_{11}	CH_3	CF_3	A	49[c]
	5b	n-C_5H_{11}	CH_3	n-C_5F_{11}	A	49[c]
4c	**5c**	n-C_3H_7	CH_3	n-C_7F_{15}	A	52[c]
4d	**5d**	n-C_5H_{11}	t-Bu	CF_3	A	79
	5e	n-C_5H_{11}	t-Bu	n-C_5F_{11}	A	90
4f	**5f**	n-C_3H_7	t-Bu	n-C_5F_{11}	d	60
4g	**5g**	CH_3CH=CH	t-Bu	n-C_5F_{11}	A	57
4h	**5h**	n-C_3H_7-CH=CH	t-Bu	n-C_5F_{11}	A	63
4i	**5i**	PhCH=CH	t-Bu	n-C_3F_7	A	83
4j	**5j**	C_6H_5	t-Bu	n-C_5F_{11}	B	64
4k	**5k**	4-F-C_6H_4	t-Bu	n-C_5F_{11}	B	58
4l	**5l**	4-MeO-C_6H_4	t-Bu	n-C_5F_{11}	B	64

[a] Method A: via F-organolithium (Scheme II); method B: via F-organomagnesium bromide (Scheme III). [b] Pure, isolated product. In all cases, GLC yields are quantitative. [c] Very sensitive to hydrolysis. The yields refer to the amount of distilled product obtained with >90% purity. [d] F-Organomagnesium bromide was used: 4 h at −45 °C and then 3 days at rt.

Scheme III

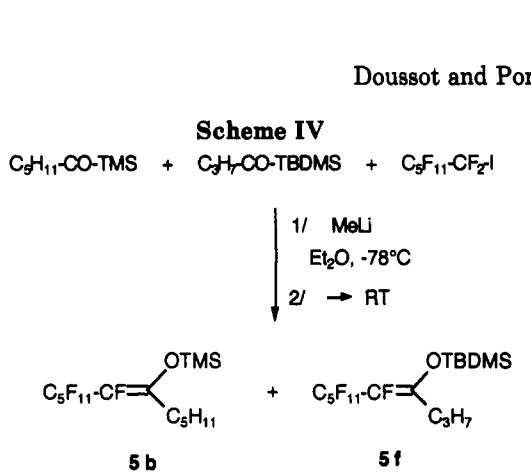


the enone, and even TBDMS substitution was not able to stop completely the reaction at the enoxysilane level. Thus the choice of magnesium reagent is crucial to optimize the formation of aromatic **5**. It was also shown that TMS derivatives are not stable to hydrolysis.[8] Hence the optimized conditions to prepare aromatic **5** are those reported in Scheme III: the perfluoroorganomagnesium, more stable than its lithium analogue, is prepared by halogen–metal exchange at −45 °C,[10] prior to the addition of the aroyl-*tert*–butyldimethylsilane. The temperature was allowed to rise after completion of the nucleophilic addition step. With TBDMS substitution and magnesium as counterion, the subsequent nucleophilic attack on silicon by fluoride was no more effective than the hydrolysis, and good isolated yields of aryl enoxysilanes **5j–l** were obtained (Table I).

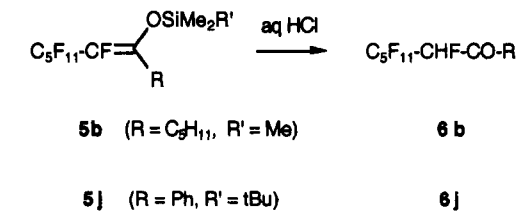
In contrast to aliphatic analogues, aromatic analogues of **5** are obtained as a mixture of two diastereomers in a ratio ~85/15 (GLC and NMR).

We have already discussed the intramolecular character of the reaction sequence leading to perfluoroalkenyl ketones[8] and hence to the aromatic enoxysilane **5**. The following experiment, depicted in the Scheme IV, provides further demonstration that there is no elimination of $Me_2R'SiF$ from the alkoxide adduct. Two different acylsilanes, distinguishable by their acyl and their trialkylsilyl moieties, were mixed with perfluorohexyl iodide and treated by methyllithium according to our standard procedure. GLC analysis demonstrated the exclusive formation of **5b** and **5f**, without any trace of crossed products. Hence it is clear that intermolecular silyl transfer to an intermediate enolate did not take place and that enoxysilanes **5** arose from a Brook rearrangement–β–elimination sequence in both the aliphatic (at least using

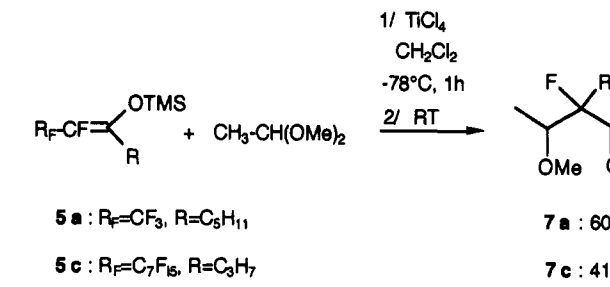
Scheme IV



Scheme V



Scheme VI



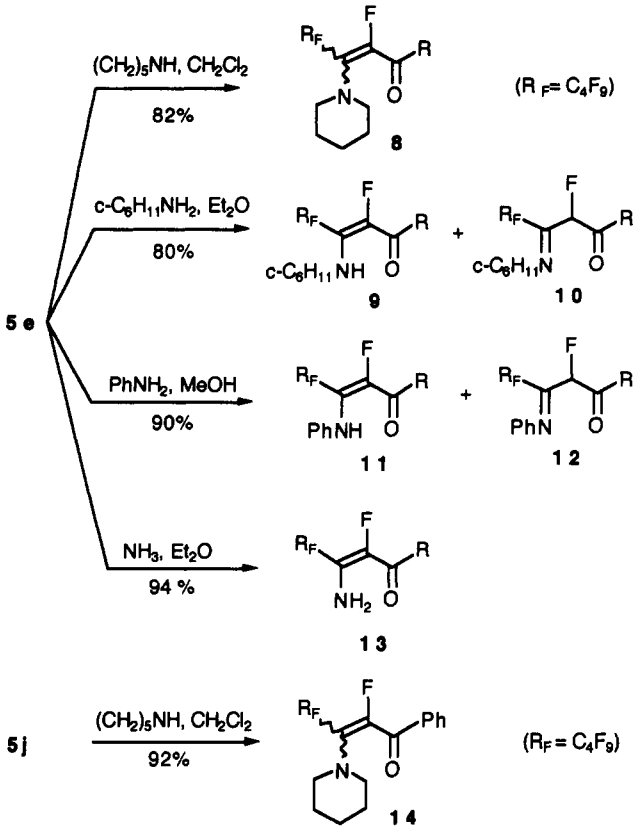
lithium reagents) and the aromatic series (at least using magnesium reagents).[8]

Perfluoroenoxysilanes 5 as Enolate Equivalents. Hydrolysis. As mentioned above, TMS derivatives are much more easily hydrolyzed than their TBDMS analogues. Acid workup of the reaction mixture from hexanoyltrimethylsilane with perfluorohexyllithium led directly to the 1–hydroperfluorohexylpentylketone **6b** in 80% isolated yield (Scheme V). The TBDMS analogue **5e** resisted diluted aqueous HCl and an excess of hydrofluoric acid in acetonitrile. After treatment during 2 days with THF–1 M HCl 1/1, 84% of **5e** was recovered; compound **5e** was hydrolyzed in 79% yield (GLC) after treatment during 7 days with THF–concd HCl (**6b** was characterized in the crude state by ^{1}H NMR (δ Hα ~5 ppm, J_{HF} = 47 Hz)). The aromatic enoxysilanes behave similarly: TBDMS derivative **5j** needed several days of treatment with concd HCl in THF whereas the TMS analogue was very easily hydrolyzed with dilute aqueous HCl.

Aldol-Type Reactions. Some enoxysilanes **5** were submitted to the aldol reaction under the Mukaiyama conditions.[11] No reaction was observed with either TBDMS **5** or with aldehydes (PhCHO or CH_3CHO). When a ketal was used as electrophile, aldol reaction took place with TMS derivatives, as depicted in the Scheme VI: compound **5a** was converted into **7a** as a mixture of two diastereomers separable by flash chromatography. The ratio (62/38) indicated a poor diastereoselectivity. Simi-

(11) Mukaiyama, T.; Banno, K.; Narasaka, K. *J. Am. Chem. Soc.* **1974**, *96*, 7503.

Scheme VII



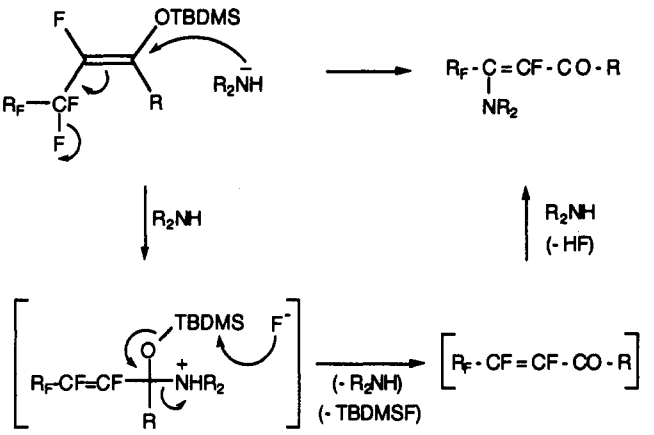
larly, **5c** gave **7c** as a mixture (58/42) of nonseparable diastereomers.

Perfluoroenoxysilanes 5 as Electrophiles: Reactions with Amines. Compounds **5** reacted much more easily with amines than with electrophiles as exemplified by reaction of aliphatic **5e** and aromatic **5j** (Scheme VII) . Treated with piperidine in dichloromethane, **5e** was smoothly converted into the β-enaminone **8**. Primary amines and ammonia reacted similarly. Cyclohexylamine gave a tautomeric mixture of enamino ketone **9** and imino ketone **10**. The prototropy was slow enough to allow their separation. Even less nucleophilic aniline gave high yield of the mixture **11** + **12** (nonseparable) although the reaction was much slower and needed warming in methanol as solvent. Enamino ketone **13** was obtained by simply bubbling gaseous ammonia into a solution of **5e** in ether. The same reaction occurred with aromatic compound **5j** which is converted with high yield into the enaminone **14** with piperidine.

This very clean and easy transformation involves interesting mechanistic aspects. (i) Almost quantitative formation of the enamino ketone needed 1 equiv of amine, and the reaction occurred as easily with TBDMS **5** as with TMS **5**, excluding initial nucleophilic attack on silicon. (ii) A similar reaction with aromatic compounds excludes also a reaction of amine as a base abstracting the α proton with subsequent displacement of the β-fluoride. Consequently, we consider that the most probable mechanism proceeds as depicted in the Scheme VIII, by an $S_{N'}$-type displacement of the β–fluoride. The resulting ammonium leaving group facilitates the nucleophilic substitution at silicon, giving an enone which reacts as expected with amines by an addition–elimination sequence.

To illustrate the convenience of this reactivity, we have performed the synthesis of **8** in a one-pot manner.

Scheme VIII



Compound **8** was obtained in 81% yield after simply adding piperidine (4 equiv) before the workup of the reaction mixture leading to **5e**. Excess amine is necessary here to obtain a good yield, probably because some alkylation by methyl iodide (from metal–halogen exchange reaction) occurred.

Summary

1-Alkyl or 1-aryl-1-[(trialkylsilyl)oxy]perfluoroalk-1-enes **5** have been preparatively synthesized from acylsilanes and perfluoroorganometallic reagents. Conditions were optimized by varying the metal (Li for aliphatics, Mg for aromatics). TBDMS derivatives are stable compounds whereas TMS ones are very easily hydrolyzed. The electron-withdrawing properties of fluorine are able to counteract the normal nucleophilic character of enoxysilanes. Hence, compounds **5** behave both as enolate equivalents (hydrolysis, aldol-type reactions) and as electrophilic substrates (reactions with amines). In particular, owing to the easy access to β-enaminones, we can consider enoxysilanes **5** as synthetic equivalents of perfluoroalk-1-enyl alkyl ketones or their corresponding β-keto esters. The most obvious extension of this chemistry will be in the application to the synthesis of heterocycles, which will be the object of forthcoming papers, as well as the chemistry of conjugated compounds **5g–i**.

Experimental Section

General informations concerning spectral data, solvents purification, and handling of organometallic reagents have been reported elsewhere.[12]

Starting Acylsilanes 4. Synthesis and characteristics of the acylsilanes **4a–f** and **4j** were already reported.[12] The same procedure was used for **4k** and **4l**. Conjugated unsaturated acylsilane **4i** was prepared by a similar methodology (aldehyde → dithiane → silyldithiane → acylsilane) except for the last step. The use of chloramine-T is unadapted here and the deprotection was carried out by treatment with CuO–$CuCl_2$[13] with 61% yields. **4g** and **4h** were prepared from the corresponding saturated acylsilane by α-selenenylation followed by oxidation–elimination according to a classical procedure[15] with an overall yield of 45%. Compounds **4g** and **4i** have been described.[14]

(12) Dondy, B.; Doussot, P.; Portella, C. *Synthesis* **1992**, 995.
(13) Stütz, P.; Stadler, P. A. *Organic Syntheses*; Wiley: New York, 1988; *Collect. Vol. VI* 109.
(14) Nowick, J. S.; Danheiser, R. L. *J. Org. Chem.* **1989**, *54*, 2798.
(15) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.
(16) Portella, C.; Iznaden, M. *J. Fluorine Chem.* **1991**, *51*, 1.

***tert*-Butyldimethylsilyl pent-1-enyl ketone (4h):** ^{1}H NMR δ 0.20 (s, Si(CH_3)$_2$), 0.90 (s, SiC(CH_3)$_3$), 1.48 (sext, J = 7 Hz, C$H_{2\beta}$), 2.17 (q, J = 7 Hz, C$H_{2\gamma}$), 6.32 (d, J = 16 Hz, CH_α), 6.64 (dt, J = 16 Hz, J = 7 Hz, CH_β); ^{13}C NMR δ -6.0 (Si(CH_3)$_2$), 13.6 (CH_3), 16.5 (C(CH$_3$)$_3$), 21.4 (C_δ), 26.5 (C(CH_3)$_3$), 34.6 (C_γ), 136.6 (C_α), 146.4 (C_β), 235.5 (CO); IR (CHCl$_3$) 1630, 1570, 840 cm^{-1}; MS m/z (%) 212 (M$^+$, 0.5), 73 (100). Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.86; H, 11.39. Found: C, 67.40; H, 11.50.

(4-Fluorobenzoyl)(*tert*-butyl)dimethylsilane (4k): ^{1}H NMR δ 0.31 (m, Si(CH_3)$_2$), 0.89 (s, SiC(CH_3)$_3$), 7.07 (2H, Ar), 7.79 (2H, Ar); ^{13}C NMR δ -4.9 (Si(CH_3)$_2$), 16.7 (SiC(CH$_3$)$_3$), 26.6 (C(CH_3)$_3$), 115.4, 130.0 and 139.2 (Ar), 165.2 (d, J = 255 Hz, C_{Ar}F), 233.0 (CO); ^{19}F NMR δ -106.4; IR (CHCl$_3$) 1610, 1580, 1075, 845 cm^{-1}; MS m/z (%) 238 (M$^+$, 0.1), 73 (100). Anal. Calcd for $C_{18}H_{19}FOSi$: 65.50; H, 8.03. Found: C, 65.35; H, 8.05.

(4-Methoxybenzoyl)(*tert*-butyl)dimethylsilane (4l): ^{1}H NMR δ 0.37 (s, Si(CH_3)$_2$), 0.96 (s, C(CH_3)$_3$), 3.84 (s, CH_3O), 6.93 (2H, Ar), 7.82 (2H, Ar); ^{13}C NMR δ -4.6 (Si(CH_3)$_2$), 16.8 (C(CH$_3$)$_3$), 26.7 (C(CH_3)$_3$), 55.3 (CH$_3$O), 113.6, 129.9, 136.6 and 163.0 (Ar), 232.5 (CO); IR (CHCl$_3$): 1610, 1580, 1165, 1070, 845 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O_2Si$: C, 67.15; H, 8.85. Found: C, 67.04; H, 9.08.

Synthesis of Enoxysilanes (5a-f). General Procedure. To a mixture of acylsilane (20 mmol) and perfluoroalkyl iodide (24 mmol) in anhydrous ether (100 mL) cooled to -78 °C was added dropwise a 1.6 M solution of MeLi-LiBr in ether (24 mmol). After 0.5 h of stirring at -78 °C, the mixture was allowed to warm to rt. After 1 h the reaction mixture was washed with water. The ether layer was decanted and dried over Mg(SO$_4$). After evaporation of the solvent, the enoxysilane was purified by distillation or a rapid chromatography over silica gel (petroleum ether). Yields were reported in Table I. Owing to their low stability, analysis of TMS derivatives were not performed, however, the structure of a representative compound (**5b**) was confirmed by HRMS.

1-(Tetrafluoroethylidene)-1-[(trimethylsilyl)oxy]hexane (5a): ^{1}H NMR δ 0.23 (s, Si(CH_3)$_3$), 0.90 (t, J = 7 Hz, CH_3), 1.30 (m, 4H), 1.50 (m, C$H_{2\beta}$), 2,17 (m, C$H_{2\alpha}$); ^{13}C NMR δ 0.14 (Si(CH$_3$)$_3$), 13.7 (CH$_3$), 22.3 (C_δ), 26.0 (C_β), 30.2 (C_α), 31.0 (C_γ), 143.6 (d, J = 10 Hz, CO); ^{19}F NMR δ -64.5 (d, J = 12 Hz, CF$_3$), -157.8 (q, J = 12 Hz, CF); IR (CHCl$_3$) 1685, 1255, 850 cm^{-1}.

1-(Perfluorohexylidene)-1-[(trimethylsilyl)oxy]hexane (5b): ^{1}H NMR δ 0.25 (s, Si(CH_3)$_3$), 0.90 (t, J = 7 Hz, CH_3), 1.35 (m, 4H), 1.55 (quint, J = 7 Hz, C$H_{2\beta}$), 2.20 (m, C$H_{2\alpha}$); ^{13}C NMR δ -0.04 (Si(CH$_3$)$_3$), 13.7 (CH$_3$), 22.5 (C_δ), 26.5 (C_β), 30.6 (C_α), 31.4 (C_γ), 134.5 (dt, J = 235 Hz, J = 30 Hz, $C_{\alpha'}$), 147.1 (d, J = 10 Hz, CO); ^{19}F NMR δ -81.4 (s, CF$_3$), -112.9 (m, CF$_{2\beta'}$), -123.4 (m, CF$_{2\gamma'}$), -124.0 (m, CF$_{2\delta'}$), -126.7 (m, CF$_{2\omega'}$), -155.2 (m, CF); MS m/z (%) 472 (M$^+$, 2), 73 (100); IR (CHCl$_3$) 1675, 1240, 855 cm^{-1}; HRMS calcd for $C_{15}H_{20}F_{12}OSi$ 472.1092, found 472.1097.

1-Propyl-1-[(trimethylsilyl)oxy]perfluorononene (5c): ^{1}H NMR δ 0.23 (s, Si(CH_3)$_3$), 0.92 (t, J = 7 Hz , CH_3), 1.54 (sext, J= 8 Hz, C$H_{2\beta}$), 2.25 (m, C$H_{2\alpha}$); ^{13}C NMR δ -0.02 (Si(CH$_3$)$_3$), 13.2 (CH$_3$), 19.7 (CH$_{2\beta}$), 32.1 (CH$_{2\alpha}$), 146.5 (d, J = 10 Hz, CO); ^{19}F NMR δ -81.6 (t, J = 10 Hz, CF$_3$), -112.9 (m, CF$_{2\beta'}$), -122.6 (m, CF$_{2\gamma'}$), -122.7 (m, CF$_{2\delta'}$), -123.4 (m, CF$_{2\epsilon'}$), -124.0 (m, CF$_{2\zeta'}$), -126.8(m,CF$_{2\omega'}$), -155.0 (m, CF); IR (CHCl$_3$) 1670, 1230, 850 cm^{-1}; MS m/z (%) 544 (M$^+$, 16), 77 (100), 73 (99).

1-(Tetrafluoroethylidene)-1-[(*tert*-butyldimethylsilyl)oxy]hexane (5d): ^{1}H NMR δ 0.20 (s, SiCH_3), 0.21 (s, SiCH_3), 0.90 (t, J = 7 Hz, CH$_3$), 0.97 (s, SiC(CH$_3$)$_3$), 1.33 (m, 4H), 1.56 (quint, J = 7 Hz, C$H_{2\beta}$), 2.20 (m, CH$_{2\alpha}$); ^{13}C NMR δ -4.8 (SiCH$_3$), -4.7 (SiCH$_3$), 13.9 (CH$_3$), 18.3 (C(CH$_3$)$_3$), 22.3 (C_δ), 25.5 (C(CH$_3$)$_3$), 26.3 (C_β), 30.5 (C_α), 31.1 (C_γ), 121.3 (dd, J = 270 Hz, J = 38 Hz, CF$_3$), 134.8 (dq, J = 235 Hz, J= 40 Hz, CF), 143.8 (d, J = 10 Hz, CO); ^{19}F NMR δ -64.3 (d, J = 12 Hz, CF$_3$), -157.5 (q, J = 12 Hz, CF); IR (CHCl$_3$) 1680, 1180, 1130, 840 cm^{-1}; MS m/z (%) 315 (M$^+$ + 1, 3), 295 (86), 105 (99), 77 (99), 73 (100). Anal. Calcd for $C_{14}H_{26}OSiF_4$: C, 53.48; H, 8.33. Found: C, 53.49; H, 8.27.

1-Perfluorohexylidene-1-[(*tert*-butyldimethylsilyl)oxy]hexane (5e): ^{1}H NMR δ 0.22 (s, SiCH_3), 0.23 (s, SiCH_3), 0.96 (t, J = 7 Hz, CH_3), 1.02 (s, SiC(CH_3)$_3$), 1.35 (m, C$H_{2\delta}$), 1.37 (m, C$H_{2\gamma}$), 1.62 (quint., J = 7 Hz, C$H_{2\beta}$), 2.23 (m, C$H_{2\alpha}$); ^{13}C NMR δ -4.9 (SiCH$_3$), -4.9 (SiCH$_3$), 13.8 (C_ω), 18.5 (SiC(CH$_3$)$_3$), 22.5 (C_δ), 25.6 (SiC(CH$_3$)$_3$), 26.8 (C_β), 30.9 (C_α), 31.5 (C_γ), 134.5 (dt, J = 235 Hz, J= 30 Hz, $C_{\alpha'}$), 147.2 (d, J = 9 Hz, CO); ^{19}F NMR δ -81.3 (m, CF$_3$), -112.9 (m, CF$_{2\beta'}$), -123.4 (m, CF$_{2\gamma'}$), -124.0 (m, CF$_{2\delta'}$), -126.7 (m, CF$_{2\omega'}$), -154.9 (m, CF); IR (CHCl$_3$) 1675, 1220, 840 cm^{-1}; MS m/z (%) 514 (M$^+$, 8), 400 (99), 257 (88), 77 (99), 73 (99), 57 (100). Anal. Calcd for $C_{18}H_{26}OSiF_{12}$: C, 42.02; H, 5.09; F, 44.31. Found: C, 41.99; H, 5.06; F, 44.38.

1-Propyl-1-[(*tert*-butyldimethylsilyl)oxy]perfluoroheptene (5f): ^{1}H NMR δ 0.19 (s, SiCH_3), 0.20 (s, SiCH_3), 0.90 (t, J= 7 Hz, CH_3), 0.95 (s, SiC(CH_3)$_3$), 1.60 (sext, J = 7 Hz, C$H_{2\beta}$), 2.18 (m, C$H_{2\alpha}$); ^{13}C NMR δ -4.9 (SiCH$_3$), -4.8 (SiCH$_3$), 13.3 (CH$_3$), 18.4 (C(CH$_3$)$_3$), 20.1 (C_β), 25.5 (C(CH$_3$)$_3$), 32.5 (C_α), 134.1 (dt, J = 235 Hz, J = 30 Hz, $C_{\alpha'}$), 146.7 (d, J = 10 Hz, CO); ^{19}F NMR δ -81.4 (t, J = 10 Hz, CF$_3$), -112.7 (m, CF$_{2\beta'}$), -123.4 (m, CF$_{2\gamma'}$), -124.0 (m, CF$_{2\delta'}$), -126.7 (m, CF$_{2\omega'}$), -154.6 (m, CF); IR (CHCl$_3$) 1665, 1220, 830 cm^{-1}; MS m/z (%) 486 (M$^+$, 1), 77 (99), 73 (100). Anal. Calcd for $C_{16}H_{22}OSiF_{12}$: C, 39.51; H, 4.56. Found: C, 39.63; H, 4.45.

Synthesis of Enoxysilanes (5g-i). The same procedure as above was applied to the conjugated acylsilanes **4g-i**, except that the workup was carried out directly after 0.25 h at -78 °C. Yields are reported in the Table I.

1-(Prop-1-enyl)-1-[(*tert*-butyldimethylsilyl)oxy]perfluoroheptene (5g): ^{1}H NMR δ 0.18 (s, SiCH_3), 0.19 (s, SiCH_3), 1.00 (s, SiC(CH_3)$_3$), 1.84 (d, J = 7 Hz, CH$_3$), 6.13 (d, J = 15 Hz, CH_α), 6.35 (dq, J = 15 Hz, J = 7Hz, CH_β); ^{13}C NMR δ -4.7 (SiCH$_3$), -4.6 (SiCH$_3$), 18.2 (CH$_3$), 18.7 (SiC(CH$_3$)$_3$), 25.7 (SiC(CH$_3$)$_3$), 120.9 (C_α), 133.3 (C_β), 135.0 (dt, J = 242 Hz, J = 30 Hz, $C_{\alpha'}$), 142.8 (d, J = 13 Hz, CO); ^{19}F NMR δ -81.34 (t, J = 10 Hz, CF$_3$), -112.6 (m, CF$_{2\beta'}$), -123.4 (m, CF$_{2\gamma'}$), -123.8 (m, CF$_{2\delta'}$), -126.7 (m, CF$_{2\omega'}$), -152.3 (m, CF); IR (CHCl$_3$) 1655, 1620, 1230, 845 cm^{-1}; MS m/z (%) 484 (M$^+$, 1), 77 (100). Anal. Calcd for $C_{16}H_{20}OSiF_{12}$: C, 39.67; H, 4.16. Found: C, 39.36; H, 3.95.

1-(Pent-1-enyl)-1-[(*tert*-butyldimethylsilyl)oxy]perfluoroheptene (5h): ^{1}H NMR δ 0.20 (s, Si(CH_3)$_2$), 0.94 (t, J = 7 Hz, CH_3), 0.97 (s, SiC(CH_3)$_3$), 1.48 (sext, J = 7 Hz, C$H_{2\delta}$), 2.16 (q, J = 7 Hz, C$H_{2\gamma}$), 6.15 (d, J = 15 Hz, CH_α), 6.38 (dt , J = 15 Hz, J = 7 Hz, CH_β); ^{13}C NMR δ -4.6 (Si(CH$_3$)$_2$), 13.5 (CH$_3$), 18.7 (C(CH$_3$)$_3$), 22.1 (C_δ), 25.8 (C(CH$_3$)$_3$), 34.8 (C_γ), 119.7 and 119.6 (C_α, isom Z and E), 134.7 (dt, J = 242 Hz, J = 30 Hz, $CF_{\alpha'}$), 138.3 and 138.4 (CH_β, isom Z and E), 142.9 (d, J = 13 Hz, CO); ^{19}F NMR δ -81.3 (t, J = 10 Hz, CF$_3$), -112.6 (m, CF$_{2\beta'}$), -123.4 (m, CF$_{2\gamma'}$), -123.8 (m, CF$_{2\delta'}$), -126.7 (m, CF$_{2\omega'}$), -152.3 (m, CF); IR (CHCl$_3$) 1655, 1620, 1200, 845 cm^{-1}; MS m/z (%) 512 (M$^+$, 8), 77 (100). Anal. Calcd for $C_{18}H_{24}OSiF_{12}$: C, 42.19; H, 4.72. Found: C, 41.92; H, 4.70.

3-[(*tert*-Butyldimethylsilyl)oxy]-1-phenyl-4,5,5,6,6,7,7,7-octafluorohepta-1,3-diene (5i). ^{1}H NMR δ 0.08 (s, SiCH_3), 0.09 (s, SiCH_3), 0.90 (s, SiC(CH_3)$_3$), 6.65 (dm, J = 15 Hz, CHα), 7.02 (d, J = 15 Hz, CHβ), 7.07 and 7.30 (m, Ph); ^{13}C NMR δ -4.56 and -4.64 (Si(CH$_3$)$_2$), 18.7 (C(CH$_3$)$_3$), 25.8 (C(CH$_3$)$_3$), 117.5 (t, J = 6 Hz, Cα), 127.2, 128.8, 128.9, and 135.8 (Ar), 134.9 (d, J = 12 Hz, Cβ), 143.2 (CO); ^{19}F NMR δ -81.1 (t, J = 9 Hz, CF$_3$), -113.4 (m, CF$_{2\delta}$), -128.0 (m, CF$_{2\gamma}$), -148.6 (m, CF); IR (CHCl$_3$) 1640, 1610, 1220, 845 cm^{-1}; MS m/z (%) 446 (M$^+$, 14), 77 (100). Anal. Calcd for $C_{19}H_{22}OSiF_8$: C, 51.12; H, 4.97. Found: C, 51.29; H, 4.77.

Synthesis of Aromatic Enoxysilanes (5j-l). To a solution of perfluorohexyl iodide (6 mmol) in anhydrous ether (17 mL) cooled to -45 °C was added 3 M ethylmagnesium bromide in ether (6 mmol). After 0.5 h at -45 °C the aroylsilane **4j-l** (5 mmol) in ether (10 mL) was added. The temperature of the reaction mixture was allowed to rise to rT. After 7 h at rT the mixture was treated as above. Silica gel chromatography gave the enoxysilanes (petroleum ether), and further elution gave small amounts of the addition alcohol (8-16%) and/or the starting aroylsilane (0-7%). Yields of enoxysilanes **5j-l** are reported in the Table I. The following data concern the major diastereomer.

1-Phenyl-1-[(*tert*-butyldimethylsilyl)oxy]perfluoroheptene (5j). This compound has been described elsewhere.[8]

1-(4-Fluorophenyl)-1-[(*tert*-butyldimethylsilyl)oxy]perfluoroheptene (5k): ^{1}H NMR δ 0.07 (s, Si(CH_3)$_2$), 0.90 (s, SiC(CH_3)$_3$), 7.07 (m, 2H), 7.34 (m, 2H); ^{13}C NMR δ -4.7 (Si(CH$_3$)$_2$), 18.2 (C(CH$_3$)$_3$), 25.4 (C(CH$_3$)$_3$), 115.0, 129.1, and 131.0 (Ar), 135.7 (dt, J = 244 Hz, J= 29 Hz, $C_{\alpha'}$), 144.7 (d, J = 12 Hz, CO), 163.6 (d, J = 249 Hz, C_{Ar}F); ^{19}F NMR δ -81.6 (t, J = 12 Hz, CF$_3$), -111.1 (m, ArF), -111.6 (q, J = 12 Hz, CF$_{2\beta'}$), -122.7 (m, CF$_{2\gamma'}$), -123.6 (m, CF$_{2\delta'}$), -126.8 (m, CF$_{2\omega'}$), -151.2 (quint, J= 12 Hz, CF); IR

($CHCl_3$) 1665, 1600, 1230, 850 cm^{-1}; MS *m/z* (%) 538 (M^+, 1), 77 (100). Anal. Calcd for $C_{19}H_{19}OSiF_{13}$: C, 42.38; H, 3.56. Found: C, 42.44; H, 3.54.

1-(4-Methoxyphenyl)-1-[(*tert*-butyldimethylsilyl)oxy]-perfluoroheptene (5l): ^1H NMR δ 0.04 (s, $Si(CH_3)_2$), 0.90 (s, $SiC(CH_3)_3$), 3.85 (s, OCH_3), 6.90 (m, 2H), 7.28 (m, 2H); ^{13}C NMR δ -4.7 ($Si(CH_3)_2$), 18.3 ($C(CH_3)_3$), 25.3 ($C(CH_3)_3$), 55.2 (OCH_3), 113.4, 125.1, and 130.4 (Ar), 135.3 (dt, J = 242 Hz, J = 29 Hz, $CF_{\alpha'}$), 146.0 (d, J = 12 Hz, *C*O), 160.7 ($C_{Ar}OMe$); ^{19}F NMR δ -81.4 (m, CF_3), -111.3 (m, $CF_{2\beta'}$), -122.6 (m, $CF_{2\gamma'}$), -123.5 (m, $CF_{2\delta'}$), -126.8 (m, $CF_{2\omega'}$), -152.2 (m, *C*F); IR ($CHCl_3$) 1665, 1610, 1230, 845 cm^{-1}; MS *m/z* (%) 550 (M^+, 4), 369 (98), 77 (100). Anal. Calcd for $C_{20}H_{22}O_2SiF_{12}$: C, 43.64; H, 4.03. Found: C, 43.77; H, 3.87.

Hydrolysis of Enoxysilanes 5. Hydrolysis of 5b: 1-hydroperfluorohexylpentylketone (6b). The procedure described for the synthesis of **5a–f** was applied to the acylsilane **4a** and perfluorohexyl iodide, but the reaction mixture was treated with 2 M aqueous HCl. **6b** was obtained with 80% yield after chromatographic purification (petroleum ether–CH_2Cl_2 85/15): ^1H NMR δ 0.92 (t, J = 7 Hz, CH_3), 1.34 (m, 4H), 1.67 (m, $CH_{2\beta}$), 2.72 (m, $CH_{2\alpha}$), 5.10 (ddd, J = 48 Hz, J = 19 Hz, J = 4 Hz, *C*HF); ^{13}C NMR δ 13.7 (CH_3), 22.3, 31.0, 39.4, and 40.8 ($(CH_2)_4$), 88.7 (dt, J = 201 Hz, J = 28 Hz, $C_{\alpha'}$), 200.0 (d, J = 24 Hz, *C*O); ^{19}F NMR δ -81.4 (t, J = 10 Hz, CF_3), -118.9 (dm, J = 140 Hz, $F_{\beta'}$), 120.6 (dm, J = 140 Hz, $F_{\beta'}$), -122.5 (m, $CF_{2\gamma'}$), -123.2 (m, $CF_{2\delta'}$), -126.7 (m, $CF_{2\epsilon'}$), -205.3 (dm, J = 48 Hz, CHF); IR ($CHCl_3$) 1740, 1200 cm^{-1}; MS *m/z* (%) 400 (M^+, 25), 77 (100). Anal. Calcd for $C_{12}H_{12}OF_{12}$: C, 36.01; H, 3.02; F, 56.97. Found: C, 36.64; H, 3.03; F, 56.96.

Hydrolysis of 5j: 1-Hydroperfluorohexylphenylketone (6j). The procedure described for the synthesis of **5g–j** was applied to perfluorohexyl iodide and the aroylsilane **4j**, but the reaction mixture was treated with 2 M aqueous HCl, leading to **6j** [8] with a 75% yield.

Aldol Type Reactions. 3-Fluoro-2-methoxy-3(-trifluoromethyl)nonan-4-one (7a). To **5a** (0.496 g, 1.82 mmol) in CH_2Cl_2 (22.5 mL) cooled to -78 °C were added 1,1-dimethoxyethane (0.21 mL, 2.01 mmol) and $TiCl_4$ (0.22 mL, 2.01 mmol). After 1 h at -78°C the mixture was left to warm up rT overnight. The reaction mixture was washed with water. The organic layer was dried over $Mg(SO_4)$. After evaporation of the solvent and purification over silica gel (petroleum ether–CH_2Cl_2 80/20), **7a** (0.28 g, 60%) was obtained as a mixture of two diastereomers (62/38): ^1H NMR δ 0.88 (t, J = 7 Hz, CH_3), 1.18 (d, J = 6 Hz, CH_3CH), 1.28 (m, 4H), 1.57 (quint, J = 7 Hz, $CH_{2\beta}$), 2.63 (m, $CH_{2\alpha}$), 3.22 (s, OCH_3 minor isom), 3.38 (s, OCH_3 maj isom), 3.90 (dq, J = 23 Hz, J = 7 Hz, $CHOCH_3$); ^{13}C NMR (maj isom) δ 13.0 (CH_3CH), 13.7 (CH_3CH_2), 21.8 (C_β), 22.3 (C_γ), 30.8 (C_δ), 39.5 (C_α), 57.7 (OCH_3), 76.7 (d, J = 20 Hz, *C*H), 121.1 (dq, J = 286 Hz, J = 30 Hz, *C*F), 203.4 (d, J = 28 Hz, *C*O); ^{19}F NMR (maj and minor isom) δ -74.1 and -74.5 (m, CF_3), -186.6 and -195.0 (d, J = 23 Hz, *C*F); IR ($CHCl_3$) 1730, 1190, 1100 cm^{-1}; MS *m/e* 259 (M^+ + 1, 0.7), 59 (100). Anal. Calcd for $C_{11}H_{18}O_2F_4$: C, 51.16; H, 7.03. Found: C, 50.79; H, 7.34.

3-Fluoro-2-methoxy-3-(perfluoroheptyl)heptan-4-one (7c). Starting from **5c**, the same procedure gave **7c** (two diastereomers, 58/42) with 41% yield after chromatographic purification (petroleum ether–CH_2Cl_2 90/10): ^1H NMR δ 0.92 (2t, J = 7 Hz, CH_3CH_2), 1.29 and 1.32 (d, J = 8 Hz, CH_3CH), 1.61 (2 sex., J = 7 Hz, $CH_{2\beta}$), 2.64 (m, $CH_{2\alpha}$), 3.22 and 3.42 (s, OCH_3), 3.95 (m, *C*H); ^{13}C NMR δ 13.3 (CH_3CH_2), 13.7 (CH_3CH), 15.7 ($CH_{2\beta}$), 41.3 and 41.9 ($CH_{2\alpha}$), 57.7 and 58.5 (OCH_3), 78.0 and 78.9 (d, J = 20 Hz, CH), 117.1 (dt, J = 289 Hz, J = 30 Hz, CF), 202.4 and 203.1 (d, J = 28 Hz, *C*O); ^{19}F NMR δ -81.4 (t, J = 12 Hz, CF_3), -115.9 (m, $CF_{2\beta'}$), -117.9 (dm, J = 295 Hz, $CF_{\gamma'}$), -120.0 (dm, J = 295 Hz, $CF_{\gamma'}$), -122.4 (m, 4F), -123.3 (m, $CF_{2\epsilon'}$), -126.7 (m, $CF_{2\omega'}$), -178.5 and -192.1 (m, *C*F); IR ($CHCl_3$) 1730, 1230, 1150 cm^{-1}; MS *m/z* (%) 530 (M^+, 57), 59 (100). Anal. Calcd for $C_{15}H_{14}O_2F_{16}$: C, 33.98; H, 2.66. Found: C, 34.14; H, 2.73.

Reactions of Enoxysilanes 5 with Amines and Ammonia. 2-Fluoro-1-(perfluorobutyl)-1-piperidinooct-1-en-3-one (8). Piperidine (0.045 g, 0.52 mmol) was added to a solution of the enoxysilane **5e** (0.268 g, 0.52 mmol) in CH_2Cl_2 (2 mL). After 40 min at rT, the mixture was washed with water. Usual workup and silica gel filtration (petroleum ether–CH_2Cl_2 80/20) gave the enaminone **8** (0.19 g, 82%) as a nonseparable mixture of two diastereomers (*Z*/*E* = 7/93 after ^1H NMR; Z and E signals were tentatively attributed by analogy with similar enaminoesters[16]): ^1H NMR δ 0.92 (t, J= 7 Hz, CH_3), 1.35 (m, 4H), 1.60 (m, 6H), 1.65 (quint, J = 7 Hz, $CH_{2\beta}$), 2.63 (td, J = 9 Hz, J = 4 Hz, $CH_{2\alpha}$), 2.90 (*E*) and 3.05 (*Z*) (m, $N(CH_2)_2$); ^{13}C NMR δ 13.7 (CH_3), 22.4 (C_β), 23.1 ($NCH_2CH_2CH_2$), 23.7 (C_γ), 26.2 (NCH_2CH_2), 31.4 (C_δ), 39.6 (C_α), 53.1 (NCH_2), 130.2 (m, $C_{\beta'}$) 151.3 (d, J= 273 Hz, $C_{\alpha'}$), 193.6 (d, J= 34 Hz, *C*O); ^{19}F NMR (maj isom.) δ -81.4 (m, CF_3), -113.2 (m, $CF_{2\alpha'}$), -122.6 (m, $CF_{2\beta'}$), -126.8 (m, $CF_{2\gamma'}$), -134.6 (m, *C*F): IR ($CHCl_3$) 1685, 1200 cm^{-1}; MS *m/z* (%) 445 (M^+, 5), 83 (100). Anal. Calcd for $C_{17}H_{21}ONF_{10}$: C, 45.85; H, 4.75; N, 3.15. Found: C, 45.61; H, 4.52; N, 3.05.

1-(Cyclohexylamino)-2-fluoro-1-(perfluorobutyl)oct-1-en-3-one (9) and 1-(Cyclohexylimino)-2-fluoro-1-(perfluorobutyl)octan-3-one (10). Cyclohexylamine (0.040 g, 0.4 mmol) was added to a solution of **5e** (0.103 g, 0.2 mmol) in ether (1 mL). After 3 days at rT, workup as above (petroleum ether–CH_2Cl_2 80/20) gave **9** (0.037 g, 43%) and **10** (0.032 g, 37%). **9**: ^1H NMR δ 0.91 (t , J = 7 Hz, CH_3), 1.30 (m, 8H), 1.63 (m, 4H), 1.75 (m, 2H), 1.90 (m, 2H), 2.60 (td, J = 7 Hz, J = 4 Hz, $CH_{2\alpha}$), 3.33 (m, *C*H), 9.05 (d, J = 8 Hz, N*H*); ^{13}C NMR δ 13.8 (CH_3), 22.4 (C_β), 23.5, 24.5, 35.0, and 54.6 (c-C_6H_{11}), 25.3 (C_γ), 31.4 (C_δ), 37.8 (C_α), 133.1 (m, *C*N), 141.5 (d, J = 240 Hz, CF), 196.4 (d, J = 30 Hz, *C*O); ^{19}F NMR δ -81.4 (m, CF_3), -109.6 (m, $CF_{2\gamma'}$), -123.3 (m, $CF_{2\delta'}$), -126.6 (m, $CF_{2\epsilon'}$), -163.8 (m, *C*F); IR ($CHCl_3$) 3720, 1725, 1530, 1200 cm^{-1}; MS *m/z* (%) 459 (M^+, 28), 240 (64), 83 (67), 55 (100). **10**: ^1H NMR δ 0.90 (t, J = 7 Hz, CH_3), 1.30 (m, 8H), 1.50–1.85 (m, 8H), 2.60–2.85 (m, $CH_{2\alpha}$), 3.50 (s, *C*H-N), 5.58 (d, J = 46 Hz, *C*HF); ^{13}C NMR δ 80.7 (d, J = 194 Hz, *C*HF), 203.5 (*C*O); ^{19}F NMR δ -81.6 (m, CF_3), -112.6 (m, $CF_{2\gamma'}$), -122.1 (m, $CF_{2\delta'}$), -125.2 (m, $CF_{2\epsilon'}$), -192.7 (d, J = 46 Hz, *C*F); IR ($CHCl_3$) 1710, 1580, 1200 cm^{-1}; MS *m/z* (%) 459 (M^+, 0.1), 83 (100). Anal. Calcd for $C_{18}H_{23}ONF_{10}$: C, 47.06; H, 5.05; N, 3.05. Found: C, 46.48; H, 4.72; N, 2.79.

1-Anilino-2-fluoro-1-(perfluorobutyl)oct-1-en-3-one (11) and 1-(Phenylimino)-2-fluoro-1-(perfluorobutyl)octan-3-one (12). A solution of aniline (0.057 g, 0.61 mmol) and **5e** (0.104 g, 0.2 mmol) in MeOH (1 mL) was refluxed overnight. Workup as above (petroleum ether–CH_2Cl_2 85/15) gave a mixture (not separated) of **11** and **12** (0.085 g, 90%, **11**/**12** = 30/70): ^1H NMR δ 0.90 (2t, J = 7 Hz, CH_3), 1.30 (m, 4H), 1.50 and 1.70 (m, $CH_{2\beta}$), 2.62 (enamino) and 2.70 (imino) (td, J = 7 Hz, J = 4 Hz, $CH_{2\alpha}$), 5.50 (d, J = 46 Hz, *C*HF), 6.90–7.40 (m, C_6H_5), 8.69 (s, N*H*); ^{13}C NMR δ 13.8 (CH_3), 22.0 (C_β), 22.4 (C_γ), 31.0 (C_δ), 38.1 (C_α), 87.2 (d, J = 196 Hz, *C*HF), 118.7, 122.7, 125.1, 126.6, 129.0, 129.2, 141.1, and 145.8 (C_{Ar}), 197.3 (imino) and 204.3 (enamino) (d, J = 24 Hz, *C*O); ^{19}F NMR δ -81.5 (m, CF_3), -109.5 (dt, J = 290 Hz, J = 10 Hz, $CF\gamma$ imino), -113.6 (dq, J = 290 Hz, J = 11 Hz, CF_γ imino), -109.8 (dt, J = 26 Hz, J = 11 Hz, $CF_{2\gamma'}$ enamino), -122.0 and -122.7 (m, $CF_{2\delta'}$), -125.7 and -126.7 (m, $CF_{2\epsilon'}$), -146.6 (quint, J = 26 Hz, *C*F enamino), -190.8 (dm, J = 46 Hz, CH*F* imino); IR ($CHCl_3$) 3660, 1720, 1595, 1200 cm^{-1}; MS *m/z* (%) 453 (M^+, 11), 99 (100). Anal. Calcd for $C_{18}H_{17}ONF_{10}$: C, 47.69; H, 3.78; N, 3.09. Found: C, 47.56; H, 3.56; N, 3.06.

1-Amino-2-fluoro-1-(perfluorobutyl)oct-1-en-3-one (13). NH_3 was bubbled into a solution of **5e** (0.122 g, 0.24 mmol) in ether (4 mL) cooled to 0 °C during 3 h. The mixture was washed with water. Normal workup and filtration over silica gel (petroleum ether–CH_2Cl_2 80/20) gave pure (*E*)-**13** (0.084 g, 94%): ^1H NMR δ 0.90 (t, J = 7 Hz, CH_3), 1.35 (m, 4H), 1.65 (quint, J = 7 Hz, $CH_{2\beta}$), 2.59 (td, J = 7.5 Hz, J = 4 Hz, $CH_{2\alpha}$), 6.25 (s, NH_2); ^{13}C NMR δ 13.9 (CH_3), 22.4 (C_β), 23.3 (C_γ), 31.4 (C_δ), 38.0 (C_α), 130.3 (dt, J = 24 Hz, J = 20 Hz, $C_{\beta'}$), 139.0 (d, J= 240 Hz, $C_{\alpha'}$), 197.9 (d, J= 29 Hz, *C*O); ^{19}F NMR δ -81.5 (t, J = 9 Hz, CF_3), -115.9 (m, $CF_{2\gamma'}$), -124.1 (m, $CF_{2\delta'}$), -126.7 (m, $CF_{2\epsilon'}$), -141.3 (m, *C*F); IR ($CHCl_3$) 3495, 3295, 1665, 1605, 1200 cm^{-1}; MS *m/z* (%) 378 (M^+ + 1, 17), 306 (100). Anal. Calcd for $C_{12}H_{13}ONF_{10}$: C, 38.21; H, 3.47; N, 3.71. Found: C, 38.27; H, 3.27; N, 3.74.

1-Phenyl-3-piperidinoperfluorohept-2-en-1-one (14). The procedure described above for the synthesis of **8** was applied to the enoxysilane **5j**, except that ether was used as solvent. Enaminone **14** (*Z*/*E* = 20/80) was obtained with 92% yield: ^1H NMR δ 1.35 (*E*) and 1.60 (*Z*) (6H), 2.76 (*E*) and 3.15 (*Z*) (4H), 7.45–8.95 (5H, Ph); ^{13}C NMR δ 23.5, 25.9, and 52.3 ($N(CH_2)_5$), 128.7, 129.0, 134.0, and 135.5 (Ph), 155.0 (d, J =183 Hz, $CF\alpha$),

187,1 (d, J = 29 Hz, CO); ^{19}F NMR δ -81.6 (CF_3), -108.7 (Z) (CF_α), -109.7 (Z) and -112.6 (E) ($CF_{2\gamma}$), -119.2 (E) (CF_α), -120.6 (Z) and -122.8 (E) ($CF_{2\delta}$), -126.8 ($CF_{2\omega}$)

One-Pot Synthesis of Enaminone 8 from Perfluorohexyl Iodide. Enoxysilane **5e** was prepared as described above from perfluorohexyl iodide. Piperidine (4 equiv) was added to the reaction mixture. After 1 h at rT, workup as described above (preparation of 8 from **5e**) gave 8 (overall yield: 81%).

Acknowledgment. We thank the "Ministère de la Recherche" for financial support and Atochem Co. (Dr. Lantz) for a generous gift of perfluoroalkyl iodides.