Mixed Organofluorine-Organosilicon Chemistry. 3. A Highly Efficient and Convenient Synthesis of Aryl Perfluoralk-1-enyl Ketones from Perfluoroalkyl Iodides and Aroylsilanes

Boniface Dondy 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

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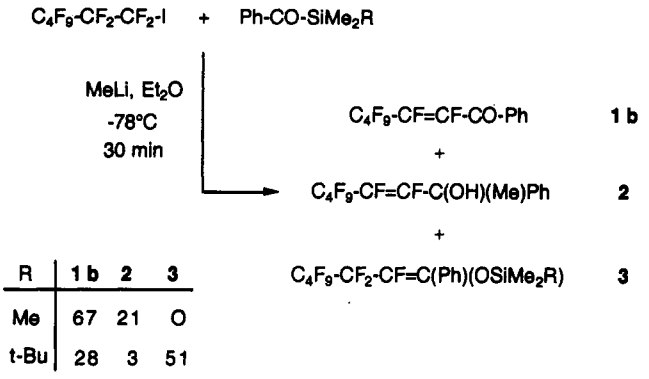
A one-pot procedure is described to synthesize aryl perfluoroalkenyl ketones with high yields from perfluoroalkyl iodides and aroylsilanes. It consists of conversion of the iodide to the perfluoroorganomagnesium bromide followed by reaction with the aroylsilane, in ether, at low temperatures (−45 °C). Warming to room temperature and addition of triethylamine accelerate the process leading quantitatively to the enones, which can be isolated in the pure *E*-configuration. The mechanism of this synthesis, involving a Brook rearrangement, is discussed. An alternative procedure is proposed to synthesize the same enones, with equivalent efficiency, from 1-aryl-1-(trimethylsilyl)perfluoroalkan-1-ols.

Perfluoroalkenyl ketones **1** are potentially useful building blocks for the synthesis of fluorine substituted compounds. They are able to undergo facile β-fluorine substitution and are excellent candidates for the synthesis of fluorinated heterocycles,[1] widely investigated as bioactive molecules. There are few preparative methods of these enones described in the literature. By far the most employed methodologies involve acylation of perfluoalkenyl organometallics.[2,3] In another approach, enones **1** were generated in situ from the corresponding enol phosphates.[1] Acylation of unsaturated perfluoroorganolithium,[4] -zinc,[5] -copper,[6] and -magnesium bromide[7] gave good results, but often needed the inconvenient and costly haloperfluoroalkenes or, for long-chain derivatives, their prior preparation. In a preliminary report, we have shown the interest of the reaction of perfluoroorganometallic reagents with benzoyltrimethylsilane,[8] the product of which depends on the metal and the reaction conditions. This paper is a full account of a straightforward, high yielding, and general synthesis of perfluoroalk-1-enyl aryl ketones **1** based on perfluoroalkyl iodides and aroylsilanes as starting materials.

Results

The addition of methyllithium to an ethereal solution of perfluorohexyl iodide[9] and benzoyltrimethylsilane at −78 °C gave, in a very fast reaction, the enone **1b** as the major product (67%). The reaction is so fast that some addition of methyllithium to the already formed enone took place, leading to (methyl)(perfluorohex-1-enyl)-(phenyl)carbinol (**2**) as a byproduct (28%) (Scheme I). It

Scheme I



R	1b	2	3
Me	67	21	0
t-Bu	28	3	51

is therefore desirable to slow down the last steps of the reaction and/or to convert quantitatively the perfluoroalkyl iodide to the organometallic derivative before reacting with the acylsilane. Under the same conditions, the reaction of benzoyl-*tert*-butyldimethylsilane gave a different spectrum of products, yielding a trace of alcohol **2** and, besides the enone **1b**, the enoxysilane **3** as the major product (Scheme I). Perfluoroalkyllithium is prepared in situ owing to its low stability and it is difficult to control the competition between reactions of comparable kinetics. In contrast, the above conditions could be fully met with the use of magnesium as the metal. The perfluoroorganomagnesium reagent was prepared by exchange with ethyl magnesium bromide,[9] and the subsequent addition of the benzoyltrimethylsilane gave a magnesium alcoholate **5** much more stable than the lithium analogue. Hydrolysis at low temperature yielded 1-phenyl-1-(trimethylsilyl)-perfluorohexanol **4**.[10] Hydrolysis after 3 h at room temperature yielded the 1-hydroperfluorohexyl phenyl ketone **7** (75%) with a small amount of enone **1b** (15%). By increasing the time of the reaction (15 h at rt), the enone **1b** was cleanly obtained, without byproducts. Finally, the reaction time could be dramatically shortened by adding triethylamine once the reaction mixture had reached room temperature.

Analysis of the crude enone by ^{19}F-NMR and GLC indicated a mixture of isomers in a ratio *Z*/*E* ~ 75/25.

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

(1) Ishihara, T.; Okada, Y.; Kuroboshi, M.; Shinozaki, T.; Ando, T. *Chem. Lett.* **1988**, 819. Ishihara, T. Jpn. Kokai Tokkyo Koho JP 01 22 855; *Chem. Abstr.* **1989**, *111*, 134144u. Ishihara, T. Jpn. Kokkai Tokkyo Koho JP 01 22 858; *Chem. Abstr.* **1989**, *111*, 134186j.

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(3) Normant, J. F. *J. Organomet. Chem.* **1990**, *400*, 19.

(4) Gillet, J. P.; Sauvêtre, R.; Normant, J. F. *Synthesis* **1986**, 355.

(5) Gillet, J. P.; Sauvêtre, R.; Normant, J. F. *Synthesis* **1986**, 538. Spawn, T. D.; Burton, D. J. *Bull. Soc. Chim. Fr.* **1986**, 876.

(6) Burton, D. J.; Hansen, S. W. *J. Am. Chem. Soc.* **1986**, *108*, 4229.

(7) Moreau, P.; Redwane, N.; Commeyras, A. *Bull. Soc. Chim. Fr.* **1984**, 117.

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

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

(10) Dondy, B.; Doussot, P.; Portella, C. *Synthesis* **1992**, 995.

0022-3263/93/1958-6671$04.00/0

Scheme II

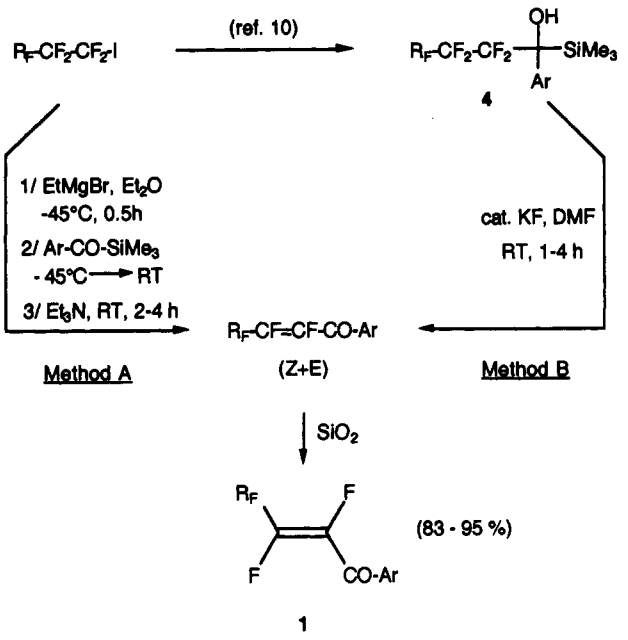


Table I. Synthesis of Aryl Perfluoroalk-1-enyl Ketone 1

			yields[a]	
R_F	Ar	product	method A[b]	method B[c]
C_2F_5	C_6H_5	**1a**	*d*	91
C_4F_9	C_6H_5	**1b**	90	88
C_6F_{13}	C_6H_5	**1c**	83	89
C_4F_9	*p*-Cl-C_6H_4	**1d**	91	88
C_4F_9	*p*-F-C_6H_4	**1e**	89	95
C_4F_9	*p*-MeO-C_6H_4	**1f**	87	92

[a] Pure, isolated *E* material. [b] Reaction time, after addition of Et_3N: 2 h for **1b–e**, 4 h for **1f**. [c] Reaction time: 1 h for **1a–c**; 2 h for **1d,e**; 4 h for **1f**. [d] Not achieved.

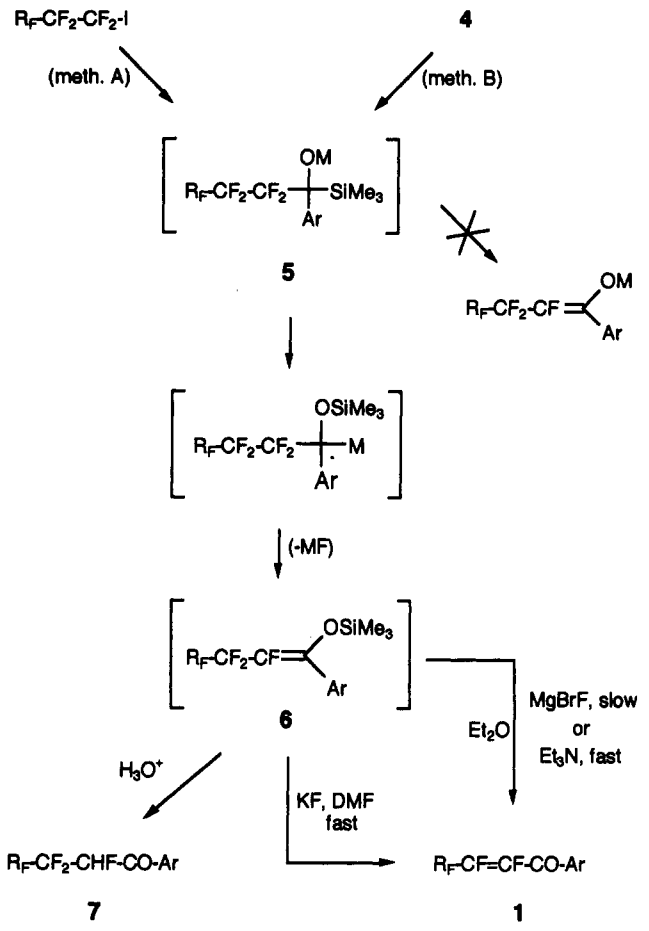
These isomers could be separated by rapid flash chromatography on silica gel, but interestingly, the major isomer after isolation had the *E* configuration, indicating a facile isomerization favored by contact with silica gel. We could isolate the essentially pure *E*-isomer by simply retarding the elution after adsorption of the crude enone on the chromatographic column. Previously reported aliphatic perfluoroenones were described as a single *E* isomer (J_{FF} = 140 Hz),[7] whereas difluoroenones are more stable in the *Z*-configuration.[11]

These optimized conditions (method A) were applied to a series of perfluoroalkyl iodides and aroylsilanes to give the corresponding *E*-enones in high yields (Scheme II and Table I).

Although this one-pot procedure is very useful and versatile, another possibility would be to start from the alcohols **4**, which were synthesized in high yields by trapping the alkoxide at low temperature.[10] Owing to the electron-withdrawing effect of the perfluoroalkyl substituent, a weak base is able to remove the hydroxylic proton to give access to the alkoxide **5** and hence to the enone. Indeed, the alcohols **4** were mildly and quantitatively converted to the corresponding enones **1** by simply adding catalytic potassium fluoride[12] to a solution of **4** in dimethylformamide (method B). Results are summarized in Scheme II and Table I. The procedure is simple and

(11) Martinet, P.; Sauvêtre, R.; Normant, J. F. *Bull. Soc. Chim. Fr.* **1990**, 86.
(12) Catalytic triethylamine worked as well to initiate the reaction.

Scheme III



efficient and thus the alcohols **4** can be considered as synthetic equivalents of the enones **1**.

Discussion

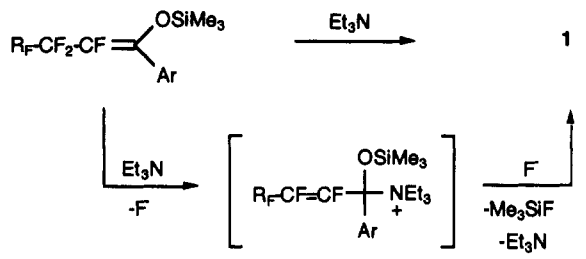
The process leading to the enone has already been proposed as a multistep pathway depicted in Scheme III. The key step is a Brook rearrangement (*C*- to *O*-silyl migration)[13] subsequent to the nucleophilic addition, followed by β-elimination[14] of the α-fluoride to give the intermediate enoxysilane **6**. The latter is further attacked by fluoride ion to yield the enone. Whether the last step is concerted or proceeds via an enolate intermediate remains undetermined. This mechanism deserves further comments and further experimental verifications.

(i) The last step is considerably slowed down if magnesium acts as the counterion in place of lithium, explaining the time of reaction and the possibility to stop it at any step.

(ii) The intermediate perfluoroenoxysilane **6** can be isolated if the silicon is hindered by a crowded *tert*-butyl substituent (Scheme I).[8,15] Although the trimethylsilyl analogue has not been isolated, its occurrence in the pathway was demonstrated by the isolation of the corresponding hydrolysis product, the 1-hydroperfluorohexyl phenyl ketone **7**, when hydrolysis was carried out after an adapted reaction time at room temperature.

(13) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77.
(14) For examples of sequential Brook rearrangement-β-elimination, see: Reich, H. J.; Holtan, R. C.; Bolm, C. *J. Am. Chem. Soc.* **1990**, *112*, 5609 and refs therein.
(15) Doussot, P.; Portella, C. *J. Org. Chem.*, following paper in this issue.

Scheme IV



(iii) The great acceleration of the last step by adding triethylamine to the reaction mixture is certainly a consequence of the electrophilic properties of the perfluoroenoxysilane.[15] A S_N'-type substitution leads to the unsaturated ammonium salt intermediate that facilitates nucleophilic attack on silicon (Scheme IV). Another reason could be complexation of the magnesium cation, making the fluoride more nucleophilic.

(iv) The intramolecular character of the process leading to the enoxysilane **6** and hence to the enone was demonstrated by the following experiment. After completion of the addition of perfluorohexylmagnesium bromide to benzoyltrimethylsilane, *tert*-butyldimethylsilyl chloride was added to the reaction mixture at −10 °C, and then the temperature was allowed to rise to room temperature for 4 h. After hydrolysis of the reaction mixture, only the 1-hydroperfluorohexyl ketone **7** (80%), accompanied by some traces of enone **1b**, was observed. No trace of the perfluoroenoxy-*tert*-butyldimethylsilane **3** could be detected, excluding the occurrence of an enolate intermediate, and hence of an elimination of trimethylsilyl fluoride at the alkoxide **5** level (Scheme III).

(v) Method B which starts from the alcohol **4** is different only by the mode of generation of the alkoxide **5**. Fluoride in DMF, with potassium as countercation, is much more nucleophilic and the whole process is much easier, allowing a rapid conversion into the enone without needing addition of triethylamine.

Conclusion

Finally, the Brook rearrangement, associated with the fluorophilicity of silicon, is the driving force of this one-pot multistep process. Owing to the availability of perfluoroalkyl iodides and the easy synthesis of the starting aroylsilanes,[10,16] this new methodology constitutes probably the most efficient and versatile synthesis of perfluoroenones **1**.

Experimental Section

General information concerning spectrometric equipment and data and chromatographic analysis have been previously reported, as have the syntheses and characterization of the starting aroylsilanes.[10] All experiments with organometallic reagents were carried out under argon, by syringe-cap techniques. Anhydrous ether was obtained by distillation over benzophenone–sodium.

Synthesis of Enones 1b–f from Perfluoroalkyl Iodides and Aroylsilanes (method A). General Procedure. A solution of perfluoroalkyl iodide (6 mmol) in ether (35 mL) was cooled to −45 °C. EtMgBr (~2 M in ether, 6 mmol) was added under stirring which was maintained at this temperature for 0.5 h. The aroylsilane (5 mmol) was added at −45 °C, the cooling bath was removed, and the mixture was allowed to rise to rt. Triethylamine (5 mmol) was added and stirring was maintained for 2–4 h. The reaction mixture was washed with 0.1 N HCl, the ether layer was decanted, dried over $MgSO_4$, and filtered, and the solvent was removed under vacuum. Chromatographic purification was performed as follows: the crude product, dissolved in the eluent (see below), was adsorbed on the head of the chromatographic column, and the elution was started 3 h later to allow a complete isomerization to the *E*-isomer. Enones were eluted with petroleum ether/CH_2Cl_2 80/20 for **1b–e**, 70/30 for **1f**. Results are summarized in Table I.

Synthesis of Enones 1a–f from the Alcohols 4a–f (method B). General Procedure. Potassium fluoride (0.05 mmol) was added to a solution of the alcohol (1 mmol) in DMF (10 mL). The mixture was stirred at rt until the complete conversion of the alcohol into the enone was indicated by TLC or GLC analysis (1–4 h). Ether extraction, after addition of dilute aqueous HCl was followed by the same purification procedure as above. Results are summarized in Table I.

(*E*)-Perfluorobut-1-enyl phenyl ketone (1a): ^{1}H NMR δ 7.4 (m, 5H); ^{13}C NMR δ 108.7 (tm, J = 286 Hz, CF_2), 118.2 (qt, J = 287 Hz, J = 36 Hz, CF_3), 128.9, 129.3, 134.2, and 134.9 (*Ph*), 142.2 (ddt, J = 266 Hz, J = 41 Hz, J = 30 Hz, CF_β), 149.1 (dd, J = 276 Hz, J = 39 Hz, CF_α), 183.2 (d, J = 25 Hz, *CO*); ^{19}F NMR δ −85.2 (m, 3F), −121.7 (ddq, J = 25.4 Hz, J = 11.5 Hz, J = 2.5 Hz, CF_2), −144.8 (dtq, J = 141 Hz, J = 25.4 Hz, J = 6.4 Hz, CF_α), −157.2 (dtq, J = 141 Hz, J = 11.4 Hz, J = 5.1 Hz, CF_β); IR 1705, 1680; MS *m/z* (%) 286 (M^+, 25), 105 (100). Anal. Calcd for $C_{11}H_5F_7O$: C, 46.17; H, 1.76. Found: C, 46.02; H, 1.55.

(*E*)-Perfluorohex-1-enyl phenyl ketone (1b): ^{1}H NMR δ 7.4 (m, 5H); ^{13}C NMR δ 129.1, 129.2, 134.3, and 135.1 (*Ph*), 142.3 (ddt, J = 270 Hz, J = 40 Hz, J = 30 Hz, CF_β), 149.3 (dd, J = 277 Hz, J = 40 Hz, CF_α), 183.6 (d, J = 24 Hz, *CO*); ^{19}F NMR δ −81.2 (t, J = 8 Hz, 3F), −118.3 (m, 2F), −124.7 (m, 2F) , −126.7 (m, 2F), −144.0 (dm, J = 142 Hz, CF_α), −155.3 (dm, J = 142 Hz, CF_β); IR 1690, 1660; MS *m/z* (%) 386 (M^+, 20), 105 (100). Anal. Calcd for $C_{13}H_5F_{11}O$: C, 40.43; H, 1.30. Found: C, 40.63; H, 1.36.

(*E*)-Perfluorooct-1-enyl phenyl ketone (1c): ^{1}H NMR δ 7.3 (m, 5H); ^{13}C NMR δ 128.9, 129.2, 134.3 and 134.9 (*Ph*), 142.3 (ddt, J = 267.4 Hz, J = 30 Hz, J = 30 Hz, CF_β), 149.2 (dd, J = 276.4 Hz, J = 39.4 Hz, CF_α), 183.4 (d, J = 23 Hz, *CO*); ^{19}F NMR δ −81.6 (m, 3F), −113.5 (m, 2F), −117.2 (m, 2 F), −121.5 (m, 4 F), −125.9 (m, 2F), −139.6 (dm, J = 138 Hz, CF_α), −158.0 (dm, J = 138 Hz, CF_β); IR 1680; 1650; MS *m/z* (%) 486 (M^+; 30), 105 (100). Anal. Calcd for $C_{15}H_5F_{15}O$: C, 37.05; H, 1.04. Found: C, 37.39; H, 1.19.

(*E*)-Perfluorohex-1-enyl 4-chlorophenyl ketone (1d): ^{1}H NMR δ 7.8 (m, 2H), 7.5 (m, 2H); ^{13}C NMR δ 129.5, 130.7, 132.5, and 141.8 (C_6H_4Cl), 142.5 (ddt, J = 269 Hz, J = 40 Hz, J = 30 Hz, CF_β), 148.9 (dd, J = 276 Hz, J = 38 Hz, CF_α), 182.1 (d, J = 26 Hz, *CO*); ^{19}F NMR δ −81.4 (m, 3F), −118.4 (m, 2F), −124.7 (s, 2F), −126.8 (m, 2F), −144.6 (dm, J = 141 Hz, CF_α), −154.3 (dm, J = 141 Hz, CF_β); IR 1720, 1690; MS *m/z* (%) 421 (M^+, 20), 309 (100). Anal. Calcd for $C_{13}H_4F_{11}OCl$: C, 37.12; H, 0.96. Found: C, 37.14; H, 0.94.

(*E*)-Perfluorohex-1-enyl 4-fluorophenyl ketone (1e): ^{1}H NMR δ 7.3 (m, 2H), 8.0 (m, 2H); ^{13}C NMR δ 116.2, 116.7, and 132.4 (C_6H_4), 139.6 (ddt, J = 269 Hz, J = 40 Hz, J = 30 Hz, CF_β), 148.1 (dd, J = 276 Hz, J = 39 Hz, CF_α), 166.8 (d, J = 258.4 Hz, $C_{ar}F$), 180.7 (d, J = 29 Hz, *CO*); ^{19}F NMR δ −81.9 (m, 3F), −101.6 (m, Ar*F*), −118.7 (m , 2F), −125.1 (m, 2F), −127.1 (m, 2F), −144.6 (dm, J = 139 Hz, CF_α), −155.3 (dm, J = 139 Hz, CF_β); IR 1705, 1670; MS *m/z* (%) 404 (M^+, 25), 281 (100). Anal. Calcd for $C_{13}H_4F_{12}O$: C, 38.69; H, 1.00. Found: C, 38.30; H, 0.90.

(*E*)-Perfluorohex-1-enyl 4-methoxyphenyl ketone (1f): ^{1}H NMR δ 7.8 (m, 2H), 7.0 (m, 2H), 3.9 (s, 3H); ^{13}C NMR δ 55.6 (OCH_3), 114.4, 126.7, and 132.2 (C_6H_4), 138.7 (ddt , J = 252 Hz, J = 50 Hz, J = 25 Hz, CF_β), 149.3 (dd, J = 282 Hz, J = 37 Hz, CF_α), 165.6 ($COCH_3$), 180.5 (d, J = 23 Hz, *CO*); ^{19}F NMR δ −81.5 (m, 3F), −118.4 (m, 2F), −124.6 (m, 2F), −126.9 (m, 2F), −142.9 (dm, J = 139.8 Hz, CF_α), −157.4 (dm, J = 139.8 Hz, CF_β); IR 1700, 1660; MS *m/z* (%) 416 (M^+, 15), 135 (100). Anal. Calcd for $C_{14}H_7F_{11}O_2$: C, 40.40; H, 1.70. Found: C, 40.37; H, 1.74.

Isolation and Characterization of the *Z*-Isomer of 1b and 1e. In a separate experiment, the same procedure as above (method A) was applied to $C_6F_{13}I$ and $PhCOSiMe_3$ or *p*-$FC_6H_4COSiMe_3$, except that the crude enone was quickly chromatographed over silica gel. After (*E*)-**1** (25–30%) and a mixture of

(16) Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647. Bullman Page, P. C.; Klair, S. S.; Rosenthal, S. *Chem. Soc. Rev.* **1990**, *19*, 147.

(*E*)-1 and (*Z*)-1 (45–50%), pure (*Z*)-1 (15–20%) was eluted. The *Z*-isomer differs from the *E*-isomer essentially by the following ^{19}F NMR signals: (*Z*)-**1b** δ −116.2 (m, 2F), −121.7 (m, 1F), −123.3 (m, 2F), −148.3 (m, 1F); (*Z*)-**1e** δ −100.9 (m, Ar*F*), −116.2 (m, 2F), −122.3 (m, 1F), −123.4 (m, 2F), −147.7 (m, 1F).

Reaction of Perfluorohexyllithium with Benzoyltrimethylsilane. A solution of benzoyltrimethylsilane (0.534 g, 3 mmol) and $C_6F_{13}I$ (1.6 g, 3.6 mmol) in ether was cooled to −78 °C. Methyllithium (1.6 M solution of MeLi–LiBr in ether, 3.6 mmol) was added. After 30 min of stirring at −78 °C, the reaction mixture was washed with dilute HCl. The ether layer was decanted and dried over $MgSO_4$. The solvent was removed under vacuum and the crude mixture was chromatographed over silica gel to give the enone **1b** (0.780 g, 67%, petroleum ether/CH_2Cl_2 80/20) and the alcohol **2** (0.253 g, 21%, CH_2Cl_2). Compound **2** has spectral characteristics in agreement with those reported for the two-carbon homologue perfluorooct-1-enylcarbinol.[17]

(Methyl)(phenyl)(perfluorohex-1-enyl)carbinol (2): ^1H NMR δ 2.2 (s, C*H*$_3$), 3.5 (s, O*H*), 7.5–8.0 (m, 5H); ^{13}C NMR δ 27.3 (*C*H$_3$), 75.0 (d, *J* = 20 Hz, *C*(OH)), 124.4, 128.4, 128.8 and 142.6 (*C*$_6$H$_5$); ^{19}F NMR δ −81.6 (m, 3F), −117.7 (m, 2F), −125.1 (m, 2F), −126.9 (m, 2F), −142.2 (dm, *J* = 138 Hz, *F*β), −165.8 (dm, *J* = 138 Hz, *F*α); MS *m/z* (%) 402 (M^+, 15), 121 (100).

Reaction of Perfluorohexyllithium with Benzoyl-*tert*-butyldimethylsilane. The same procedure gave, after silica gel separation, 1-phenyl-1-[(*tert*-butyldimethylsilyl)oxy]perfluorohex-1-ene (**3**) (0.795 g, 51%, petroleum ether/CH_2Cl_2 90/10), enone **1b** (0.324 g, 28%), and alcohol **2** (0.027 g, 3%).

(17) Moreau, P.; Albadri, R.; Redwane, N.; Commeyras, A. *J. Fluorine Chem.* **1980**, 15, 103.

1-[(*tert*-Butyldimethylsilyl)oxy]-1-phenylperfluorohept-1-ene (3): ^1H NMR δ 0.18 (s, 6H), 1.1 (s, 9H), 7.5 (m, 5H); ^{13}C NMR δ −4.7 ((*C*H$_3$)$_2$Si), 18.3 (C(*C*H$_3$)$_3$), 25.3 (*C*(CH$_3$)$_3$), 128.0, 128.9, 129.7, and 132.9 (*C*$_6$H$_5$), 135.0 (dt, *J* = 242 Hz, *J* = 30 Hz, C*F*β), 145.6 (d, *J* = 12 Hz, C*F*α); ^{19}F NMR δ−81.4 (m, 3F), −115.5 (m, 2F, maj isom), −114.5 (m, 2F, minor isom), −122.6 (m, 2F), −123.5 (m, 2F, maj isom), −123.7 (m, 2F, minor isom), −126.7 (m, 2F), −152.2 (m, *F*α, maj isom), −165.0 (m, *F*α, minor isom); MS *m/z* (%) 520 (M^+, 20), 105 (100). Anal. Calcd for $C_{18}H_{20}F_{12}OSi$: C, 43.85; H, 3.87. Found: C, 43.52; H, 4.05.

1-Hydroperfluorohexyl Phenyl Ketone (7). The method A procedure described above was applied to benzoyltrimethylsilane (0.534 g, 3 mmol) and $C_6F_{13}I$ (1.61 g, 3.6 mmol), except that the reaction mixture was quenched with 2 M HCl after 3 h at rt. The usual workup and flash chromatography (petroleum ether/CH_2Cl_2 80/20) gave **7** (0.865 g, 71%) and **1b** (0.17 g, 15%): ^1H NMR δ 5.9 (ddd, *J* = 46 Hz, *J* = 19 Hz, *J* = 4 Hz, 1H), 7.5 (m, 3H), 7.8 (m, 2H); ^{13}C NMR δ 86.7 (ddd, *J* = 201 Hz, *J* = 31 Hz, *J* = 25 Hz, *C*α), 186.2 (d, *J* = 20 Hz, *C*O); ^{19}F NMR δ −81.3 (m, 3F), −118.3 (d, *J* = 304 Hz, *F*β), −122.4 (m, 2F), −122.75 (d, *J* = 304.2 Hz, *F*β), −126.7 (m, 2F), −201.1 (m, *F*α); IR ($CHCl_3$) 1700, 1210 cm^{-1}; MS *m/z* (%) 406 (M^+, 25), 105 (100). Anal. Calcd for $C_{13}H_6F_{12}O$: C, 38.44; H, 1.49. Found: C, 38.23; H, 1.29.

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