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Oxygenative Perfluoroalkylation of Olefinic Compounds Using Perfluoroalkyl Iodide in the Presence of Oxygen

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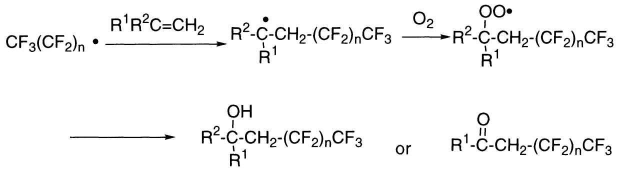
Reactions of perfluoroalkyl iodides with styrene and its derivatives were investigated under radical conditions in the presence of oxygen. The photochemical reaction of styrene with $CF_3(CF_2)_5I$ in the presence of tributyltin hydride or tris(trimethylsilyl)silane under an oxygen atmosphere afforded the corresponding perfluoroalkylated alcohols in moderate yields together with $CF_3(CF_2)_5H$. However, the photochemical reactions of styrene and its derivatives with $CF_3(CF_2)_nI$ (n = 3, 5) in the presence of hexabutylditin under oxygen produced the perfluoroalkylated alcohols in good yields. Furthermore, the reactions of styrenes with $CF_3(CF_2)_nI$ (n = 3, 5, 9) and $Na_2S_2O_4$ in the presence of a base under air formed the same alcohols in good yields. The alcohols were found to provide a novel type of α-fluoroalkylated styrenes by acidic dehydration. Perfluoroalkylated α,β-unsaturated ketones were synthesized by oxygenative perfluoroalkylations of α-chlorostyrene and its derivatives using $CF_3(CF_2)_nI$ (n = 3, 5) under radical reaction conditions. The ketones were found to be good synthetic building blocks for perfluoroalkylated heterocycles, such as pyrazoles, dihydrodiazepines, pyrimidines, and isoxazoles.

Fluoroalkylated organic molecules often show unique properties, and are widely used as medicines, pesticides, dyes, surfactants, functionalized organic materials, etc.[1] Especially, the introduction of perfluoroalkyl groups into particular positions of organic molecules may give rise to unique biological and physical properties which cannot be achieved by incorporating other functional groups.[2] Thus, the exploitation of a novel method for perfluoroalkylations of organic molecules is still an important subject in organofluorine chemistry.

Free radical reactions leading to carbon-carbon bond formation have emerged as a powerful tool in organic synthesis.[3] The radical species plays an important role in the introduction of a perfluoroalkyl group into organic molecules, and a wide variety of fluoroalkylated products can be prepared using fluoroalkyl radicals which are much more reactive for olefins than alkyl radicals.[4,5] However, the reactions of perfluoroalkyl radicals with unsaturated molecules in the presence of oxygen have rarely been employed for organic synthesis,[6] because of the high reactivity of fluoroalkyl radicals with oxygen.[7] Recently, we investigated the reaction of perfluoroalkyl iodide under radical conditions in the presence of oxygen, and found the simultaneous introduction of a perfluoroalkyl radical and molecular oxygen into olefin to give perfluoroalkylated alcohol and ketone (Scheme 1).[8,9] In this paper, we describe the perfluoroalkylation of styrene and its derivatives using perfluoroalkyl radicals in the presence of oxygen to afford oxyfluoroalkylated products which proved to be useful building blocks for α-fluoroalkylated styrenes and perfluoroalkylated heterocycles.



Scheme 1.

Results and Discussion

Oxyfluoroalkylation of Styrene and Its Derivatives. The thermal or photochemical reactions of perfluoroalkyl iodides are known to produce highly reactive perfluoroalkyl radicals which can be employed for addition to olefins and acetylenes.[10] In order to generate fluoroalkyl radicals under mild conditions and to use these highly reactive species for organic synthesis, the removal of iodine from perfluoroalkyl iodide has been investigated using single electron transfer (SET) or radical initiators, such as palladium catalysts, transition metal carbonyls, and triethylborane.[4,5,10] We attempted to use an iodine abstraction with a stannyl or silyl radical and a one-electron reduction with $Na_2S_2O_4$ to generate the perfluoroalkyl radical from perfluoroalkyl iodide.

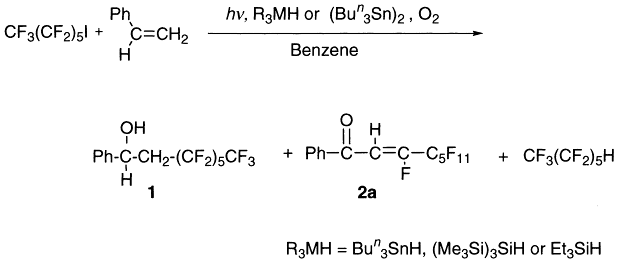
Stannyl and silyl radicals are generated under mild conditions and can sometimes be used in the presence of molecular oxygen. We thus tried a photochemical reaction of styrene with perfluoroalkyl iodide in the presence of tributyltin hydride, triethylsilane, tris(trimethylsilyl)silane, or hexabutylditin as an additive under an O_2 atmosphere (Scheme 2 and Table 1). When a solution of perfluorohexyl iodide and styrene in benzene in the presence of tributyltin hydride was irradiated using a metal halide lamp in a Pyrex tube under an O_2 atmosphere, the perfluoroalkylated alcohol **1** was obtained (Scheme 2). In runs using Bu_3SnH, an undesired reduction product, $CF_3(CF_2)_5H$, was also formed; the product ratios of **1** and $CF_3(CF_2)_5H$ varied with the used amounts of Bu_3SnH

Table 1. Oxygenative Perfluorohexylation of Styrene

Entry	Additive (mol amt.)	Conversion of $CF_3(CF_2)_5I$/%$^{a)}$	Yields/%$^{b)}$		
			1	**2a**	$CF_3(CF_2)_5H$
1	Bu_3SnH (2.3)	100	22	0	56
2	Bu_3SnH (1.1)	91	30	0	33
3	Bu_3SnH (0.56)	52	25	0	16
4	$(Me_3Si)_3SiH$ (1.1)	99	56	0	14
5	Et_3SiH (1.1)	9	0	0	0
6	$(Bu_3Sn)_2$ (2.0)	100	58	18	0
7	$(Bu_3Sn)_2$ (1.1)	51	32	8	0

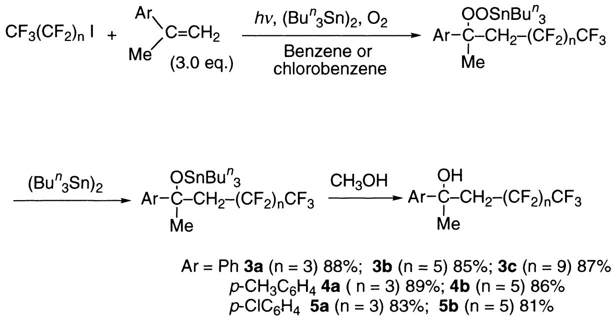
a) Determined by ^{19}F NMR. b) Determined by ^{19}F NMR based on $C_6F_{13}I$.

(Table 1, entries 1–3). The use of $(Me_3Si)_3SiH$ instead of Bu_3SnH increased the yield of **1**, probably due to the stronger Si–H bond than the Sn–H bond (entry 4).[11] However, an attempted run using Et_3SiH was unsuccessful, and 91% of the added R_FI remained unchanged in photoirradiation for 5 h (entry 5) since the Si–H bond in Et_3SiH was so very strong that the hydrogen could not be abstracted.[12] In runs using Bu_3SnH and $(Me_3Si)_3SiH$, the formation of $CF_3(CF_2)_5H$ was unavoidable. Therefore, runs in the presence of hexabutylditin ($(Bu_3Sn)_2$) instead of Bu_3SnH or $(Me_3Si)_3SiH$ were attempted. Since the ditin is known to be unreactive to a carbon radical,[13] it is expected that the perfluoroalkyl radical would not react with the ditin, but would do so with styrene selectively. Thus, a solution of $CF_3(CF_2)_5I$, styrene (3.0 mol amt.), and $(Bu_3Sn)_2$ (2.0 or 1.1 mol amt.) was photoirradiated under an O_2 atmosphere (entries 6 and 7). In this reaction, alcohol **1** and unsaturated ketone **2** were obtained without the formation of $CF_3(CF_2)_5H$.


$R_3MH = Bu^n{}_3SnH, (Me_3Si)_3SiH$ or Et_3SiH

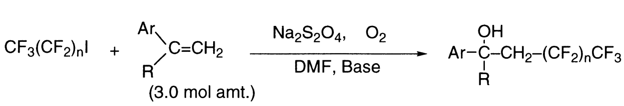
Scheme 2.

A similar reaction of α-methylstyrene gave the corresponding alcohols selectively. The photochemical reaction of perfluorohexyl iodide (1 mol amt.) with α-methylstyrene (3 mol amt.) in the presence of $(Bu_3Sn)_2$ (2.0–2.2 mol amt.) in benzene under an O_2 atmosphere was carried out. All photochemical reactions of α-methylstyrenes with perfluoroalkyl iodide proceeded smoothly to produce the corresponding alcohols in high yields, as determined by ^{19}F NMR (Scheme 3).


Ar = Ph **3a** (n = 3) 88%; **3b** (n = 5) 85%; **3c** (n = 9) 87%
p-$CH_3C_6H_4$ **4a** (n = 3) 89%; **4b** (n = 5) 86%
p-ClC_6H_4 **5a** (n = 3) 83%; **5b** (n = 5) 81%

Scheme 3. Preparation of **3**–**5**. Yields were determined by ^{19}F NMR.

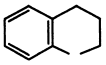
Furthermore, we investigated the oxygenative perfluoroalkylation of α-methylstyrenes without using tin compounds, since we considered that tin-free methods of generating radicals and propagating chain reactions are important in recent radical chemistry.[14] One-electron reduction of perfluoroalkyl iodide is a useful method for the formation of a perfluoroalkyl radical.[15] We attempted the oxygenative perfluoroalkylation of α-methylstyrenes initiated by a one-electron reduction of perfluoroalkyl iodide. However, because many one-electron reducing agents are reactive to oxygen, those that can be used in the presence of oxygen are limited. In this study, we attempted to use $Na_2S_2O_4$.[16] Perfluoroalkyl iodide reacted with α-methylstyrenes (3 mol amt.) in the presence of O_2 and $Na_2S_2O_4$ (2.5 mol amt.) under basic conditions (Scheme 4, Table 2). In the reactions carried out under an O_2 atmosphere, considerable perfluorohexyl iodide was left unchanged, even when excess amounts of $Na_2S_2O_4$ for perfluoroalkyl iodide were used (Table 2, entries 1 and 2). However, similar reactions in contact with the atmosphere afforded perfluoroalkylated alcohols in good yields (Table 2, entries 3–9). The isolation and purification of the alcohols proved to be easier in this procedure than in the photochemical method. Furthermore, this method was effective for a gram-scale reaction. When the reaction was carried out using 2.2 g (5 mmol) of perfluorohexyl iodide and 1.8 g (15 mmol) of α-methylstyrenes under the similar conditions, **3b** was obtained in 77% yield.


3a , b; 4b; 5b; 6

Scheme 4.

In these reactions, a perfluoroalkyl radical was produced at first by iodine abstraction from perfluoroalkyl iodide with a stannyl radical or one-electron reduction with $SO_2^{\bullet -}$ (Scheme 5, reaction 1). The perfluoroalkyl radical is known to react with both α-methylstyrene and molecular oxygen.[17,18] Howev-

Table 2. Oxygenative Perfluoroalkylation of Styrene Derivatives using $Na_2S_2O_4$

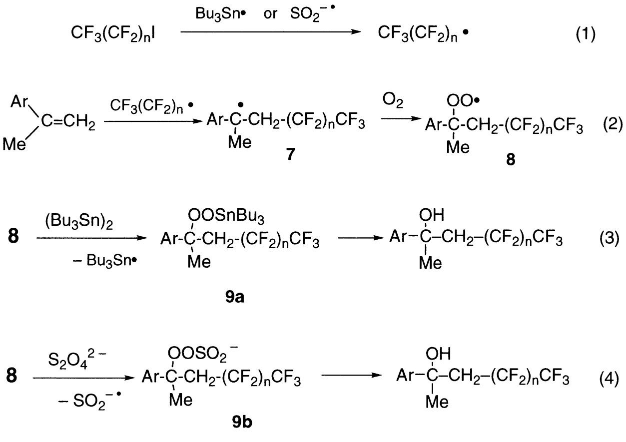
Entry	Ar, R of Ar(R)C=CH_2		Atmosphere	n of $CF_3(CF_2)_nI$	Base	Product; Yield/%[a]
1	Ph	Me	O_2	5	$NaHCO_3$	**3b**; 26[b]
2	Ph	Me	O_2	5	$NaHCO_3$	**3b**; 67[c]
3	Ph	Me	air	5	$NaHCO_3$	**3b**; 82 (70)
4	Ph	Me	air	5	Na_2HPO_4	**3b**; 85
5	Ph	Me	air	5	Et_3N	**3b**; 85
6	Ph	Me	air	3	$NaHCO_3$	**3a**; 78 (62)
7	Ph	Me	air	9	$NaHCO_3$	**3c**; 71
8	p-ClC_6H_4	Me	air	5	$NaHCO_3$	**4b**; 79 (73)
9	p-MeC_6H_4	Me	air	5	$NaHCO_3$	**5b**; 75 (67)
10			air	5	$NaHCO_3$	**6**; 78 (68)

a) Yields were determined by ^{19}F NMR based on $CF_3(CF_2)_nI$ using $PhCF_3$ as an internal standard. Isolated yield is shown in parentheses.

b) 69% of $CF_3(CF_2)_nI$ was left unchanged.

c) Reaction was carried out using 5 mol amt. of $Na_2S_2O_4$, but 20% of $CF_3(CF_2)_nI$ was left unchanged.

er, the oxyfluoroalkylation could be done selectively by choosing the reaction conditions. When the reaction was performed in the presence of more than 3 mol amt. of α-methylstyrene, the addition of the perfluoroalkyl radical to α-methylstyrene giving the cumyl-type radical **7** occurred at first, and then the radical **7** reacted with oxygen to give the peroxyl radical **8** (reaction 2). The fluoroalkylated alcohols should be formed via the peroxides **9a** and **9b** (reactions 3 and 4). The radical **7** might be very stable for the iodine abstraction from perfluoroalkyl iodide and the iodoperfluoroalkylation of α-methylstyrene did not proceed.



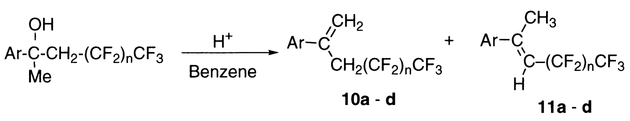
Scheme 5.

Alcohols **3**–**6** thus obtained are expected to be useful synthetic intermediates for various organofluorine compounds. In our preliminary experiments, alcohols **3**–**5** were found to provide α-fluoroalkylated styrenes **10**, which formally allow the introduction of a perfluoroalkyl group on the α-methyl carbon of α-methylstyrenes (Scheme 6). When alcohol **3a** in benzene was heated for 8 h in the presence of p-TsOH, α-fluoroalkylated styrene, **10a** was obtained as a main product with a small amount of **11a** (Table 3, entry 1). This result is inconsistent with the Saytzeff orientation. The length of the fluoroalkyl chains showed little effect on the ratio of **10**:**11** (entries 1 and 2), but the substituent groups on the aromatic rings in the alcohols affected the ratio (entries 1–4). On the other hand, in a similar reaction of **3b** in the presence of H_2SO_4, olefins **10b** and **11b** were obtained in 43% and 50% yields, respectively (entry 5). In the presence of CF_3CO_2H, the dehydration did not proceed (entry 6). When the isolated **10b** was heated in benzene in the presence of H_2SO_4, the isomerization of **10b** to **11b** occurred. The ratio of **10b** and **11b** in the equilibrium state was 46:54. The isomerization of **10b** to **11b** did not occur in the presence of p-TsOH under similar conditions. α-Fluoroalkylated styrenes like **10** have high potential as building blocks for the synthesis of fluorine compounds and as starting materials for new types of polymers.

Table 3. Preparation of Fluoroalkylated Olefins **10** and **11** from the Alcohol

Entry	Alcohol	Acid	Products	(Yield[a])
1	**3a**	p-TsOH	**10a** (83%)	**11a** (15%)
2	**3b**	p-TsOH	**10b** (83%)	**11b** (14%)
3	**4a**	p-TsOH	**10c** (54%)	**11c** (43%)
4	**5a**	p-TsOH	**10d** (84%)	**11d** (14%)
5	**3b**	H_2SO_4	**10b** (43%)	**11b** (50%)
6	**3b**	CF_3CO_2H	No Reaction	

a) Yields were determined by ^{19}F NMR using $PhCF_3$ as an internal standard.



a : Ar = Ph, n = 3; **b** : Ar = Ph, n = 5;
c : Ar = p-MeC_6H_4, n = 3; **d** : Ar = p-ClC_6H_4, n = 3

Scheme 6.

Preparation of Perfluoroalkylated Ketones as Building Blocks for Heterocycles. The building-block strategy has

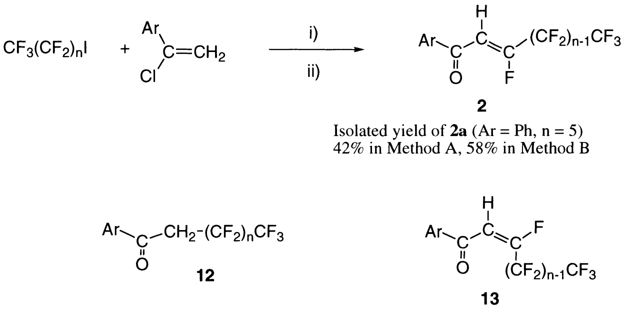
Table 4. Oxyfluoroalkylation of α-Chlorostyrenes

Entry	n of $CF_3(CF_2)_nI$	Ar of $ArC(Cl)=CH_2$	Method[a)]	Total Yield of **2**, **12** and **13**/%[b)]
1	5	Ph	A	72 (25:22:53)
2	5	Ph	B	66 (58:42:0)
3	3	Ph	A	69 (33:19:48)
4	3	Ph	B	62 (42:58:0)
5	5	p-MeC_6H_4	A	73 (22:14:64)
6	5	p-MeC_6H_4	B	67 (41:59:0)
7	5	p-ClC_6H_4	A	78 (17:27:56)
8	5	p-ClC_6H_4	B	64 (62:38:0)

a) Method A; Photochemical reaction using $(Bu_3Sn)_2$ in benzene. Method B; Reaction using $Na_2S_2O_4$ in DMF.

b) Yields were determined by ^{19}F NMR based on $CF_3(CF_2)_nI$ using $PhCF_3$ as an internal standard. The ratio of **2**:**12**:**13** was shown in parentheses.

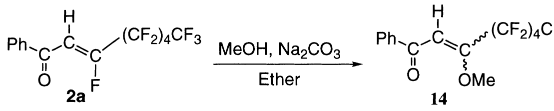
now become one of the most convenient approaches to perfluoroalkylated organic molecules, and considerable efforts have been devoted to development of the synthesis of the fluorine-containing building blocks. We considered ketones **2** to be important building blocks for fluoroalkylated heterocyclic compounds. Therefore, we attempted to develop a method for the selective synthesis of α,β-unsaturated ketones **2** and their application to the synthesis of perfluoroalkylated heterocycles.[19] After several unsuccessful attempts, we found that the ketones **2** could be obtained selectively from α-chlorostyrenes as shown in Scheme 7. In the photochemical reactions of α-chlorostyrene, fluoroalkylated ketones were obtained in 72% yield as a mixture of **2a**, **12a**, and **13a** in a ratio of 25:22:53.[20] The treatment of a mixture consisting of **2a**, **12a**, and **13a** with NEt_3 and $NaHCO_3$ in diethyl ether gave **2a** as the sole product, and **2a** was isolated in 42% yield. In this reaction, the saturated ketone **12a** was formed at first, and then the elimination of HF from **12a** occurred to afford the unsaturated ketone **2a**. Ketone **13a** should be produced by the photoisomerization of **2a**. When isolated **2a** was irradiated in benzene under similar conditions, isomerization from **2a** to **13a** was observed. Similarly, the reaction of α-chlorostyrene and perfluoroalkyl iodide using $Na_2S_2O_4$ afforded the corresponding ketones, **2a** and **12a**, in 66% as the total yield. In this procedure, the isolation and purification of ketone **2a** could be carried out more easily than in the case of photochemical reactions using ditin and **2a** was isolated in 58% yield. The attempted runs for oxyfluoroalkylation of various α-chlorostyrenes are summarized in Table 4.



Isolated yield of **2a** (Ar = Ph, n = 5)
42% in Method A, 58% in Method B

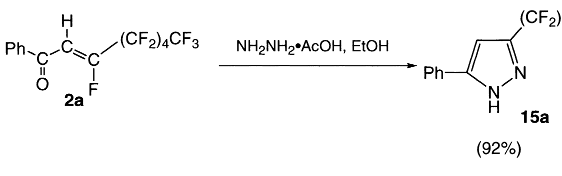
Scheme 7. *Reagent*: i) Method A: $(Bu^n{}_3Sn)_2$, $h\nu$, Benzene under O_2 atmosphere or Method B: $Na_2S_2O_4$, $NaHCO_3$, DMF under the air, rt. ii) Et_3N, Na_2CO_3, Ether, rt.

Ketone **2** is expected to be very reactive to various types of nucleophiles.[21–23] When ketone **2a**, thus obtained, was treated with methanol, a mixture of the corresponding substitution products **14** was obtained in high yield (Scheme 8). The thermodynamically more stable *Z* isomer was formed selectively. The structure of **14** was characterized by an examination of the spectral data in comparison with those of **2a** and **13**. When ketone **2a** was treated with hydrazine acetate in diethyl ether, fluoroalkylated pyrazole **15a** was obtained in 92% yield (Scheme 9). Although two tautomers, 5-aryl-3-perfluoroalkyl- and 3-aryl-5-perfluoroalkylpyrazoles, are possible, only one set of signals in the NMR spectra was observed, even at −80 °C. The ^{13}C NMR signals of the pyrazole carbon of **15a** were observed at δ 102.78, 142.52 (t), and 145.24. The observed chemical shifts were consistent with those of 5-aryl-3-perfluoroalkylpyrazole **15a** from a comparison with those of 3-phenylpyrazole (δ = 101.1 (C4), 134.5 (C3), 147.7 (C5)) and 5-phenylpyrazole (δ = 101.1 (C4), 139.3 (C3), 141. 1 (C5)) and *N*-methylpyrazole (δ = 105.2 (C4), 130.4 (C5), 138.5 (C3)) reported in the literature.[24]



Yield; 88% (*Z*: *E* = 91 : 9)

Scheme 8.



Scheme 9.

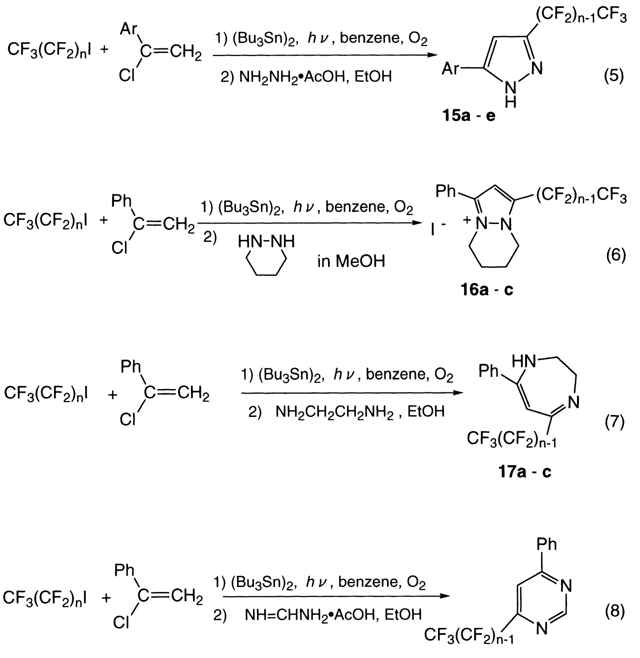
Since the photochemical reaction of α-chlorostyrenes produced a mixture of **2**, **12**, and **13**, we planned to synthesize heterocyclic compounds starting from a mixture of **2**, **12**, and **13** without their separation (Scheme 10, Table 5). By employing

Table 5. One-Pot Synthesis of Heterocycles from α-Chlorostyrenes.

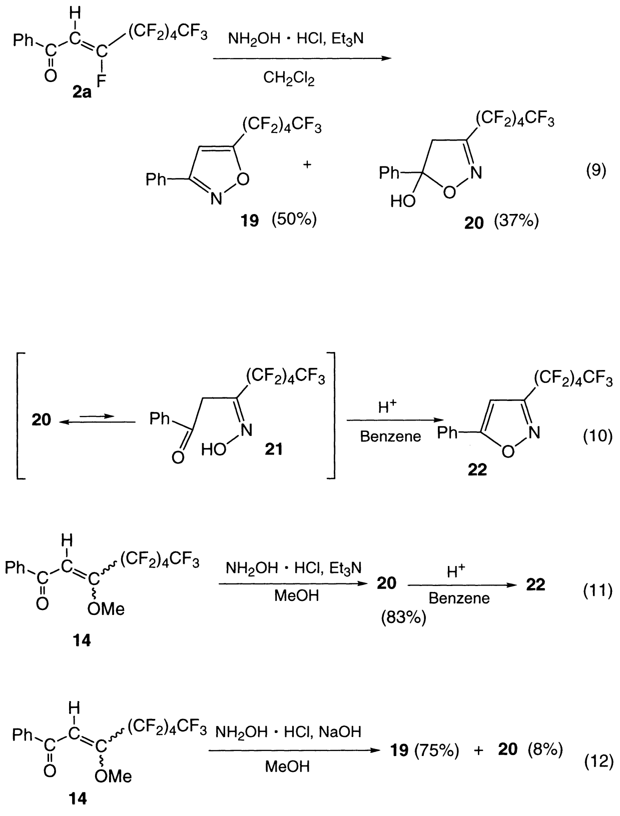
Entry	Product; *n*	Ar	Yield/%[a)]
1	**15a**; 5	Ph[b)]	65 (42)
2	**15b**; 3	Ph[b)]	59 (44)
3	**15c**; 9	Ph	69 (48)
4	**15d**; 5	p-ClC$_6$H$_4$	57 (40)
5	**15e**; 5	p-MeC$_6$H$_4$	57 (47)
6	**16a**; 3	Ph	59 (44)
7	**16b**; 5	Ph	65 (42)
8	**16c**; 9	Ph	69 (48)
9	**17a**; 3	Ph	48 (40)
10	**17b**; 5	Ph	48 (37)
11	**17c**; 9	Ph	54 (47)
12	**18a**; 3	Ph	41 (35)
13	**18b**; 5	Ph	43 (34)
14	**18c**; 9	Ph	47 (39)

a) Yields (overall yields based on $CF_3(CF_2)_nI$) were determined by ^{19}F NMR using PhCF$_3$ as an internal standard. Isolated yields are shown in parentheses.

b) Known compound.[25]



Scheme 10.



Scheme 11.

this methodology, a variety of perfluoroalkylated heterocylic compounds were prepared in short steps. When the photochemical reaction mixture was treated with hydrazine acetate, the fluoroalkylated pyrazoles **15a–e** were obtained (Scheme 10, reaction 5). The length of the fluoroalkyl chains and the substituents on the benzene ring (p-Me and p-Cl) showed little effect on the yields of the pyrazoles **15** (Table 5, entries 1–5). Interestingly, in the reaction with a cyclic hydrazine like perhydropyridazine, bicyclic iminium salts **16a–c** were obtained (Scheme 10, reaction 6; Table 5, entries 6–8). As the reaction is carried out in a one-pot procedure, the iodine atom derived from perfluoroalkyl iodide is considered to become the counter anion of the salt. The structures of these compounds were fully characterized by an examination of the spectral and analytical data. As shown in Scheme 10, dihydrodiazepines **17a–c** were obtained in moderate yields by reactions with ethylene diamine ($NH_2CH_2CH_2NH_2$) (Scheme 10, reaction 7; Table 5, entries 9–11). In this reaction, only one tautomer (7-aryl-5-perfluoroalkyl-2,3-dihydro-1*H*-1,4-diazepine: **17**) was formed; the structure was determined by a comparison of its ^{13}C-NMR spectral data with those of 5-trifluoromethy-2,3-dihydro-1,4-diazepine.[26] Similarly, pyrimidines **18a–c** were obtained in moderate yields by reactions with formamidine acetate ($NH{=}CHNH_2$•AcOH) (Scheme 10, reaction 8; Table 5, entries 12–14).

From the reaction of the ketone **2a** with hydroxylamine hydrochloride, fluoroalkylated isoxazole **19** and isoxazoline **20** were obtained in 50% and 37% yields, respectively (Scheme 11, reaction 9). The thus-obtained ^{1}H NMR chemical shift (δ_H = 7.07) of the isoxazole **19** was consistent with the reported chemical shift,[27] and the ^{13}C NMR signal of the C-5 carbon in the isoxazole ring was observed at δ = 158.83 as a triplet due to the CCF coupling reflecting the existence of a perfluoroalkyl group on this carbon. The isoxazoline **20** existed as a mixture with **21** in CDCl$_3$.[28] The isoxazole **22** (regioisomer of **19**) was obtained by heating the mixture in benzene under acidic conditions (reaction 10). On the other hand, the reaction of **14** with hydroxylamine hydrochloride in MeOH in the presence of Et$_3$N gave **20** selectively (reaction 11). Interestingly, in the reaction of **14** in the presence of NaOH, **19** formed selectively with a small amount of **20** (reaction 12). Thus, the selective synthesis of isoxazole **19** and **22** could be performed.

In summary, the high potential of ketone **2** as a building block for the synthesis of heterocyclic compounds has been demonstrated. Since α-chlorostyrenes were readily prepared from styrenes with $PhSeCl_3$,[29] or from acetophenone derivatives with PCl_5,[30] the method described here is very convenient and practical for the regioselective synthesis of various types of heterocyclic compounds bearing both perfluoroalkyl and aryl groups.

Experimental

^1H, ^{13}C, and ^{19}F NMR spectra were taken with JEOL JNM LA500 (500 MHz in ^1H, 125 MHz in ^{13}C, and 470 MHz in ^{19}F) or LA400 (400 MHz in ^1H, 100 MHz in ^{13}C) spectrometer in $CDCl_3$. Fluorine chemical shifts were determined using $PhCF_3$ as an internal standard and are given in ppm down field from external CF_3CO_2H (δ_F of $PhCF_3$ = 12.6). Mass spectra were taken with a JEOL JMS AX-505W spectrometer with a JEOL JMA 5000 mass data system using an electron-impact (EI) ionization technique at 70 eV. Gel-permeation chromatography (GPC) was performed by means of a JAI model LC-908 and a LC-918 liquid chromatograph equipped with two JAIGEL-1H columns (20 mm × 600 mm) with chloroform as an eluent.

Perfluorobutyl and -hexyl iodides were obtained from Tokyo Kasei Kogyo Co. Ltd. and purified by distillation over $Na_2S_2O_3$ prior to use. Perfluorononyl iodide was obtained from F-Tech. Inc. and was used without further purification. α-Methylstyrene and 4-chloro-α-methylstyrene were purchased from Tokyo Kasei Kogyo Co. Ltd. and were distilled prior to use. 4′-Methyl-α-methylstyrene was prepared from 4-methylacetophenone by Grignard reaction. 1,2,3,4-Tetrahydro-1-methylenenaphthalene was prepared from α-tetralone (3,4-dihydro-1(2*H*)-naphthalene) (Aldrich Chemicals) by Wittig reaction.[31] Ether refers to diethyl ether. The names of alcohols **1**, **3**, **4**, and **5**, olefins **10** and **11**, ketones **2**, **12**, **13**, and **14**, indicated by "perfluoroalkyl", are only for convenience. For example, approved names of **1**, **10a**, and **2a** in IUPAC are 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-phenyl-1-octanol, 4,4,5,5,6,6,7,7,7-nonafluoro-2-phenyl-1-heptene, and (*Z*)-3,4,4,5,5,6,6,7,7,8,8,8-decafluoro-1-phenyl-2-octen-1-one, respectively.

Photochemical Reaction of Perfluorohexyl Iodide with Styrene in the Presence of Bu_3SnH. A solution of perfluorohexyl iodide (280 mg, 0.6 mmol), styrene (1.8 mmol), and Bu_3SnH (1.38 mmol, 0.66 mmol, or 0.34 mmol) in 5 mL benzene was irradiated using a metal halide lamp (National Sky-beam MT-70) in a Pyrex tube under an oxygen atmosphere, and the reaction was monitored by ^{19}F NMR. The yields of the alcohol and $C_6F_{13}H$ were determined by ^{19}F NMR using $PhCF_3$ as an internal standard. Alcohol **1** was isolated using silica-gel column chromatography (eluted with hexane/benzene = 3/1).

2-Perfluorohexyl-1-phenylethanol 1. Colorless oil; δ_H (500 MHz) 2.34–2.65 (m, 2H), 2.50 (bs, 1H), 5.16 (dd, J = 8.55 and 3.05 Hz, 1H), 7.29–7.30 (m, 1H), 7.34–7.36 (m, 4H); δ_C (125.7 MHz) 40.03 (t, J_{CCF} = 21 Hz), 68.12, 125.80, 128.56, 129.03, 142.88; δ_F (470.4 MHz, ppm down field from external CF_3CO_2H) −5.82 (3F), −37.73 (d, J = 270 Hz, 1F), −38.63 (d, J = 270 Hz, 1F), −46.69 (2F), −47.79 (2F), −48.53 (2F), −51.07 (2F); IR (neat) 3480 cm^{-1} (OH); Found: *m*/*z* M^+, 440.0456, $C_{13}H_{11}F_9O$ requires 440.0446.

Typical Procedure for the Synthesis of Alcohols 3–6. A solution of perfluorobutyl iodide (280 mg, 0.6 mmol), α-methylstyrene (220 mg, 1.8 mmol), and $(Bu_3Sn)_2$ (770 mg, 1.2 mmol) in 5 ml benzene was irradiated in a Pyrex tube under oxygen atmosphere until the iodide was completely consumed as monitored by ^{19}F NMR (about 5 h). The reaction mixture was treated with Ph_3P (80 mg, 0.3 mmol) in MeOH (1 mL) at room temperature for 30 min to ensure conversion of small amounts of the remaining stannyl peroxide to the corresponding alcohol, and the yield of the alcohol was determined by ^{19}F NMR using $PhCF_3$ as an internal standard. Separation of alcohol **3a** from the reaction mixture was performed by silica-gel column chromatography (eluted with hexane/benzene = 3/1). Crude **3a**, which contained small amounts of tin compounds, was further purified by gel permeation chromatography.

Typical Procedure for the Oxyfluoroalkylation Initiated by One-Electron Reduction with $Na_2S_2O_4$. A mixture of perfluorohexyl iodide (0.5 mmol) and α-methylstyrene (1.5 mmol) in DMF (5 mL) was stirred overnight at room temperature in the presence of $Na_2S_2O_4$ (1.25 mmol) and $NaHCO_3$ (1.25 mmol) under air. The reaction mixture was poured into 10 mL of water and the solution was acidified to pH 3.0 by addition of aqueous HCl. From the resulting solution, organic products were extracted with ether (3 × 10 mL). The combined extracts were washed with 5% aqueous $NaHCO_3$, then with water two times and dried over $MgSO_4$. After removal of the solvent, column chromatography of the residue on aluminum oxide (hexane–benzene as gradient eluent from 50 : 50 to 0 : 100) gave the alcohol **3b** in 70% yield.

1-Perfluorobutyl-2-phenyl-2-propanol 3a. Colorless oil; NMR δ_H (500 MHz) 1.77 (s, 3H), 2.25 (s, 1H, OH), 2.49–2.69 (m, 2H), 7.28–7.31 (m, 1H), 7.33–7.36 (m, 2H), 7.47–7.50 (m, 2H); δ_C (125.7 MHz) 30.21, 42.53 (t, J_{CCF} = 20 Hz), 72.82, 124.31, 127.41, 128.47, 146.51; δ_F (470.4 MHz, ppm down field from external CF_3CO_2H) −6.41 (3F), −35.38 (d, J = 267 Hz, 1F), −37.76 (d, J = 267 Hz, 1F), −49.30 (2F), −50.69 (2F); IR (neat) 3588 cm^{-1} (OH); Found: *m*/*z* M^+, 354.0668, $C_{13}H_{11}F_9O$ requires 354.0667.

1-Perfluorohexyl-2-phenyl-2-propanol 3b. Colorless oil; NMR δ_H (500 MHz) 1.77 (s, 3H), 2.28 (s, 1H, OH), 2.52–2.72 (m, 2H), 7.27–7.30 (m, 1H), 7.36–7.39 (m, 2H), 7.47–7.51 (m, 2H); δ_C (125.7 MHz) 30.21, 42.63 (t, J_{CCF} = 19 Hz), 72.82, 124.31, 127.41, 128.45, 146.52; δ_F (470.4 MHz, ppm down field from external CF_3CO_2H) −5.50 (3F), −35.07 (d, J = 275 Hz, 1F), −37.57 (d, J = 267 Hz, 1F), −46.32 (2F), −47.52 (2F), −48.34 (2F), −50.69 (2F); IR (neat) 3588 cm^{-1} (OH); Found: *m*/*z* M^+, 454.0639, $C_{15}H_{11}F_{13}O$ requires 454.0602.

1-Perfluorodecyl-2-phenyl-2-propanol 3c. Colorless oil; NMR δ_H (500 MHz) 1.77 (s, 3H), 2.25 (s, 1H, OH), 2.52–2.72 (m, 2H), 7.28–7.31 (m, 1H), 7.37–7.40 (m, 2H), 7.46–7.49 (m, 2H); δ_C (125.7 MHz) 30.23, 42.58 (t, J_{CCF} = 20 Hz), 72.88, 124.35, 127.44, 128.49, 146.54; δ_F (470.4 MHz, ppm down field from external CF_3CO_2H) −5.46 (3F), −35.42 (d, J = 254 Hz, 1F), −36.86 (d, J = 254 Hz, 1F), −45.65 (2F), −46.07 (8F), −46.92 (2F), −47.83 (2F), −50.69 (2F); IR (neat) 3588 cm^{-1} (OH); Found: *m*/*z* M^+, 654.0457, $C_{19}H_{11}F_{21}O$ requires 654.0475.

1-Perfluorobutyl-2-(*p*-tolyl)-2-propanol 4a. Colorless oil; NMR δ_H (500 MHz) 1.74 (s, 3H), 2.30 (s, 1H, OH), 2.34 (s, 3H), 2.49–2.70 (m, 2H), 7.17 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H); δ_C (125.7 MHz) 30.12, 42.45 (t, J_{CCF} = 20 Hz), 72.73, 124.26, 129.11, 137.10, 143.68; δ_F (470.4 MHz, ppm down field from external CF_3CO_2H) −6.10 (3F), −35.45 (d, J = 266 Hz, 1F), −37.72 (d, J = 266 Hz, 1F), −49.48 (2F), −50.60 (2F); IR (neat) 3588 cm^{-1} (OH); Found: *m*/*z* M^+, 368.0871, $C_{14}H_{13}F_9O$ requires 368.0823.

1-Perfluorohexyl-2-(*p*-tolyl)-2-propanol 4b. Colorless oil; NMR $\delta_{\rm H}$ (500 MHz) 1.75 (s, 3H), 2.24 (s, 1H, OH), 2.35 (s, 3H), 2.49–2.70 (m, 2H), 7.17 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H); $\delta_{\rm C}$ (125.7 MHz) 30.21, 42.59 (t, $J_{\rm CCF}$ = 20 Hz), 72.80, 124.30, 129.18, 137.15, 143.72; $\delta_{\rm F}$ (470.4 MHz, ppm down field from external CF_3CO_2H) −5.48 (3F), −35.18 (d, J = 269 Hz, 1F), −37.66 (d, J = 269 Hz, 1F), −46.23 (2F), −47.53 (2F), 48.35 (2F), −50.79 (2F); IR (neat) 3588 cm^{-1}; Found: *m*/*z* M$^+$, 468.0714, $C_{16}H_{13}F_{13}O$ requires 468.0758.

2-(*p*-Chlorophenyl)-1-perfluorobutyl-2-propanol 5a. Colorless oil; NMR $\delta_{\rm H}$ (500 MHz) 1.75 (s, 3H), 2.27 (s, 1H, OH), 2.51–2.72 (m, 2H), 7.34 (d, J = 8.6 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H); $\delta_{\rm C}$ (125.7 MHz) 30.35, 42.42 (t, $J_{\rm CCF}$ = 20 Hz), 72.55, 125.95, 128.57, 133.34, 144.91; $\delta_{\rm F}$ (470.4 MHz) (ppm down field from external CF_3CO_2H) −6.11 (3F), −35.39 (d, J = 285 Hz, 1F), −37.76 (d, J = 285 Hz, 1F), −49.34 (2F), −50.69 (2F); IR (neat) 3588 cm^{-1} (OH); Found: *m*/*z* M$^+$, 388.0274, $C_{13}H_{10}ClF_9O$ requires 388.0277.

2-(*p*-Chlorophenyl)-1-perfluorohexyl-2-propanol 5b. Colorless oil; NMR $\delta_{\rm H}$ (500 MHz) 1.75 (s, 3H), 2.17 (s, 1H, OH), 2.49–2.69 (m, 2H), 7.34 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H); $\delta_{\rm C}$ (125.7 MHz) 30.39, 42.54 (t, $J_{\rm CCF}$ = 20 Hz), 72.60, 125.98, 128.60, 133.46, 144.93; $\delta_{\rm F}$ (470.4 MHz, ppm down field from external CF_3CO_2H) −5.95 (3F), −35.13 (d, J = 283 Hz, 1F), −37.56 (d, J = 283 Hz, 1F), 46.58 (2F), −47.77 (2F), −48.44 (2F), −51.11 (2F); IR (neat) 3482 cm^{-1} (OH); Found: *m*/*z* M$^+$, 488.0215, $C_{15}H_{10}ClF_{13}O$ requires 488.0212.

1-Tridecafluoroheptyl-1,2,3,4-tetrahydronaphthalen-1-ol 6. Yellow oil; NMR $\delta_{\rm H}$ (500 MHz) 1.84 (m, 1H), 1.95 (m, 1H), 2.05 (m, 1H), 2.13 (s, 1H, OH), 2.40 (m, 1H), 2.50–2.75 (m, 2H), 2.82 (m, 2H), 7.10–7.14 (m, 1H), 7.23–7.26 (m, 2H), 7.55–7.58 (m, 1H); $\delta_{\rm C}$ (125.7 MHz) 19.71, 29.46, 36.29, 40.45 (t, $J_{\rm CCF}$ = 20.6 Hz), 71.47, 125.98, 126.67, 127.94, 129.26, 136.23, 140.96; $\delta_{\rm F}$ (470.4 MHz, ppm down field from external CF_3CO_2H) −5.87 (3F), −34.84 (d, J = 240 Hz, 1F), −36.68 (d, J = 240 Hz, 1F), −46.32 (2F), −47.57 (2F), −48.23 (2F), −50.94 (2F); IR (neat) 3451 cm^{-1} (OH); Found: *m*/*z* M$^+$, 480.0752, $C_{17}H_{13}F_{13}O$ requires 480.0759.

Synthesis of α-Fluoroalkylated Styrene 10. Alcohol **3b** (0.2 mmol) and *p*-toluenesulfonic acid (0.02 mmol) in 10 mL of benzene were heated under reflux for 8 h. The reaction mixture was washed with 5% aqueous $NaHCO_3$, then with water, and dried over $MgSO_4$. After removal of the solvent, column chromatography of the residue on silica gel (hexane, then hexane–benzene (10 : 1)) gave pure styrene **10b** and **11b**.

3-Perfluorobutyl-2-phenylpropene 10a. Colorless oil; NMR $\delta_{\rm H}$ (500 MHz) 3.28 (t, $J_{\rm HF}$ = 20 Hz, 2H), 5.37 (s, 1H), 5.64 (s, 1H), 7.30–7.39 (5H); $\delta_{\rm C}$ (125.7 MHz) 36.17 (t, $J_{\rm CCF}$ = 20 Hz), 120.56, 126.12, 128.03, 128.51, 137.02, 140.33; $\delta_{\rm F}$ (470.4 MHz, ppm down field from external CF_3CO_2H) −5.71 (3F), −37.24 (2F), −48.68 (2F), −50.57 (2F); Found: *m*/*z* M$^+$, 336.0563, $C_{13}H_9F_9$ requires 336.0562.

3-Perfluorohexyl-2-phenylpropene 10b. Colorless oil; NMR $\delta_{\rm H}$ (500 MHz) 3.28 (t, $J_{\rm HF}$ = 20 Hz, 2H), 5.38 (s, 1H), 5.64 (s, 1H), 7.26–7.40 (5H); $\delta_{\rm C}$ (125.7 MHz) 36.25 (t, $J_{\rm CCF}$ = 20 Hz), 120.55, 126.10, 128.00, 128.48, 137.03, 140.31; $\delta_{\rm F}$ (470.4 MHz, ppm down field from external CF_3CO_2H) −5.67 (3F), −36,94 (2F), −46.52 (2F), −47.59 (2F), −47.75 (2F), −50.90 (2F); Found: *m*/*z* M$^+$, 436.0459, $C_{15}H_9F_{13}$ requires 436.0497.

3-Perfluorobutyl-2-(*p*-tolyl)propene 10c. Colorless oil; NMR $\delta_{\rm H}$ (500 MHz) 2.35 (s, 3H), 3.26 (t, $J_{\rm HF}$ = 18 Hz, 2H), 5.32 (s, 1H), 5.61 (s, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H); $\delta_{\rm C}$ (125.7 MHz) 21.11, 36.09 (t, $J_{\rm CCF}$ = 22 Hz), 119.73, 125.94, 129.18, 136.74, 137.38, 137.89; $\delta_{\rm F}$ (470.4 MHz, ppm down field from external CF_3CO_2H) −5.70 (3F), −37.29 (2F), −48.71 (2F), −50.60 (2F); Found: *m*/*z* M$^+$, 350.0695, $C_{14}H_{11}F_9$ requires 350.0716.

2-(*p*-Chlorophenyl)-3-perfluorobutylpropene 10d. Colorless oil; NMR $\delta_{\rm H}$ (500 MHz) 3.25 (t, $J_{\rm HF}$ = 18 Hz, 2H), 5.34 (s, 1H), 5.62 (s, 1H), 7.32 (4H); $\delta_{\rm C}$ (125.7 MHz) 36.18 (t, $J_{\rm CCF}$ = 22 Hz), 121.16, 127.42, 128.65, 133.94, 135.98, 138.67; $\delta_{\rm F}$ (470.4 MHz, ppm down field from external CF_3CO_2H) −5.69 (3F), −37.18 (2F), −48.67 (2F), −50.60 (2F); Found: *m*/*z* M$^+$, 370.0146, $C_{13}H_8F_9Cl$ requires 370.0170.

1-Perfluorobutyl-2-phenylpropene 11a. Colorless oil; NMR $\delta_{\rm H}$ (500 MHz) 2.31 (s, 3H), 5.76 (t, $J_{\rm HF}$ = 16 Hz, 1H), 7.36–7.42 (m, 5H); $\delta_{\rm C}$ (100.4 MHz) 17.83, 113.76 (t, $J_{\rm CCF}$ = 23 Hz), 126.15, 128.62, 129.04, 141.83, 151.34; $\delta_{\rm F}$ (470.4 MHz, ppm down field from external CF_3CO_2H) −5.68 (3F), −39.26 (2F), −48.96 (2F), −50.38 (2F).

1-Perfluorohexyl-2-phenylpropene 11b. Colorless oil; NMR $\delta_{\rm H}$ (500 MHz) 2.32 (s, 1H), 5.76 (t, $J_{\rm HF}$ = 15 Hz, 1H), 7.37–7.43 (m, 5H); $\delta_{\rm C}$ (125.7 MHz) 17.76, 113.89 (t, $J_{\rm CCF}$ = 24 Hz), 126.17, 128.62, 129.05, 141.88, 151.32; $\delta_{\rm F}$ (470.4 MHz, ppm down field from external CF_3CO_2H) −5.67 (3F), −30.15 (2F), −46.39 (2F), −47.61 (2F), −48.17 (2F), −50.94 (2F).

1-Perfluorobutyl-2-(*p*-tolyl)propene 11c. Colorless oil; NMR $\delta_{\rm H}$ (500 MHz) 2.29 (s, 3H), 2.37 (s, 3H), 5.74 (t, $J_{\rm HF}$ = 16 Hz, 1H), 7.18 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H); $\delta_{\rm C}$ (125.7 MHz) 17.73, 21.16, 112.88 (t, $J_{\rm CCF}$ = 23 Hz), 126.07, 129.29, 138.87, 139.20, 151.13; $\delta_{\rm F}$ (470.4 MHz, ppm down field from external CF_3CO_2H) −5.68 (3F), −29.98 (2F), −48.94 (2F), −50.38 (2F); Found: *m*/*z* M$^+$, 350.0725, $C_{14}H_{11}F_9$ requires 350.0716.

2-(*p*-Chlorophenyl)-1-perfluorobutylpropene 11d. Colorless oil; NMR $\delta_{\rm H}$ (500 MHz) 2.30 (s, 3H), 5.74 (t, $J_{\rm HF}$ = 16 Hz, 1H), 7.32–7.38 (m, 4H); $\delta_{\rm C}$ (125.7 MHz) 17.78, 114.16 (t, $J_{\rm CCF}$ = 23 Hz), 127.50, 128.83, 134.76, 135.14, 140.12; $\delta_{\rm F}$ (470.4 MHz, ppm down field from external CF_3CO_2H) −5.66 (3F), −30.42 (2F), −48.94 (2F), −50.39 (2F).

Typical Procedure for the Synthesis of the Unsaturated Ketone. A solution of perfluorohexyl iodide (0.40 mmol), α-chlorostyrene (1.20 mmol), and $(Bu_3Sn)_2$ (0.44 mmol) in benzene (3 mL) was irradiated using a metal halide lamp (National Sky-beam MT-70) in a Pyrex tube under an O_2 atmosphere for 5 h. In order to consume the perfluoroalkyl iodide completely, 1.1 mol amt. of $(Bu_3Sn)_2$ was required. The reaction mixture was evaporated and the residue was dissolved in ether (2 mL). After the addition of Et_3N (1 mL) and $NaHCO_3$ (130 mg), the mixture was stirred for 2 h at room temperature. Ketone **2a** was isolated in 42% yield using silica-gel column chromatography (hexane–benzene as gradient eluent from 100 : 0 to 50 : 50), followed by gel permeation chromatography.

(*Z*)-3-Fluoro-3-perfluoropentyl-1-phenyl-2-propen-1-one 2a. $\delta_{\rm H}$ (500 MHz) 6.73 (d, $J_{\rm HF}$ = 31.7 Hz, 1H), 7.51–7.55 (m, 2H, Ph), 7.60–7.63 (m, 1H, Ph), 7.88–7.91 (m, 2H, Ph); $\delta_{\rm C}$ (125.7 MHz) 110.67, 128.73, 129.00, 134.39, 136.23, 151.69 (d, $J_{\rm CF}$ = 284 Hz), 186.29; $\delta_{\rm F}$ (470.4 MHz, ppm down field from external CF_3CO_2H) −5.92 (3F), −37.14 (1F), −43.43 (2F), −47.81 (4F), −51.32 (2F); Found: *m*/*z* M$^+$ 418.0224, $C_{14}H_6F_{12}O$ requires 418.0226.

2-Perfluorohexylacetophenone 12a. From the photochemical reaction mixtures of α-chlorostyrene with perfluorohexyl iodide, saturated ketone **12a** was isolated by column chromatography and then by gel permeation chromatography. NMR δ_H (500 MHz) 3.78 (t, J_{HF} = 17.7 Hz, 2H), 7.50–7.54 (m, 2H, Ph), 7.62–7.66 (m, 1H, Ph), 7.94–7.97 (m, 2H, Ph); δ_C (100.4 MHz) 38.69 (t, J_{CCF} = 21 Hz), 128.60, 128.93, 134.19, 136.43, 189.58; δ_F (470.4 MHz, ppm down field from external CF_3CO_2H) −5.92 (3F), −36.10 (2F), −46.86 (2F), −47.87 (4F), −51.26 (2F); Found *m*/*z* 438.0263, $C_{14}H_7F_{13}O$ requires 438.0289.

(*E*)-3-Fluoro-3-perfluoropentyl-1-phenyl-2-propen-1-one 13a. Similarly, *E*-isomer **13a** was isolated using column chromatography and gel permeation chromatography from the photochemical reaction mixture. NMR δ_H (500 MHz) 6.85 (d, J_{HF} = 20.1 Hz, 1H), 7.50–7.54 (m, 2H, Ph), 7.63–7.67 (m, 1H, Ph), 7.91–7.95 (m, 2H, Ph); δ_C (125.7 MHz) 116.24, 128.92, 129.14, 134.55, 135.76, 151.68 (d, J_{CF} = 302 Hz), 186.43; δ_F (470.4 MHz, ppm down field from external CF_3CO_2H) −5.92 (3F), −40.13 (2F), −41.36 (1F), −47.25 (2F), −47.99 (2F), −51.29 (2F).

(*Z*)-3-Perfluoropentyl-3-metoxy-1-phenyl-2-propen-1-one *Z*-14. The reaction of **2a** with MeOH was carried out in ether in the presence of Et_3N; **2a** (0.5 mmol) and Et_3N (0.1 mL) were dissolved in ether (2 mL) and MeOH (1 mL), and the solution was stirred at room temperature for 2 h. The ketone **14** was obtained as a mixture of *Z* and *E*, and only *Z* was isolated from the reaction mixture by silica-gel column chromatography. NMR δ_H (500 MHz) 3.87 (s, 3H), 6.49 (s, 1H), 7.50–7.54 (m, 2H, Ph), 7.64–7.67 (m, 1H, Ph), 7.92–7.95 (m, 2H, Ph); δ_C (125.7 MHz) 62.68, 106.08, 128.80, 128.89, 133.79, 137.32, 153.39, 186.03; δ_F (470.4 MHz, ppm down field from external CF_3CO_2H) −5.94 (3F), −41.24 (2F), −47.40 (2F), −47.99 (2F), −51.32 (2F); Found: *m*/*z* M^+ 430.0426, $C_{15}H_9F_{11}O_2$ requires 430.0420.

Typical Procedure for the Oxyfluoroalkylation Initiated by One-Electron Reduction with $Na_2S_2O_4$. A solution of perfluoroalkyl iodide (0.5 mmol) and α-chlorostyrene (1.5 mmol) in DMF (5 mL) was stirred overnight at room temperature in the presence of $Na_2S_2O_4$ and Na_2CO_3 under air. The reaction mixture was poured into 10 ml of water and the solution was acidified to pH 3.0 by the addition of aqueous HCl. From the resulting solution, organic products were extracted with ether (3 × 10 mL). The combined extracts were washed with 5% aqueous $NaHCO_3$, then with water two times and dried over $MgSO_4$. To this ether solution, Et_3N was added and the resulting solution was stirred for 2 h at room temperature. After the removal of ether, the ketone was isolated by using silica-gel column chromatography.

Typical Procedure for the One-Pot Synthesis of Pyrazole 15, Dihydrodiazepines 17, and Pyrimidines 18. A solution of perfluoroalkyl iodide (0.40 mmol), α-chlorostyrene (1.20 mmol), and $(Bu_3Sn)_2$ (0.44 mmol) in 3 mL of benzene was irradiated using a metal halide lamp in a Pyrex tube under an O_2 atmosphere for 5 h. After removal of benzene from the reaction mixture, ethanol and hydrazine acetate were added to the residue. The resultant solution was stirred under reflux for 2 h. After removal of the solvent, **15** was isolated from the reaction products using column chromatography on silica-gel with hexane–dichloromethane as an eluent, followed by gel permeation chromatography.

3-Perfluoropentyl-5-phenylpyrazole 15a. Colorless needles from hexane; mp 91.2–92.2 °C; δ_H (500 MHz) 6.82 (s, 1H), 7.42–7.50 (m, 3H), 7.57–7.61 (m, 2H), 11.05 (brs, 1H); δ_C (125.7 MHz) 102.78, 125.61, 127.94, 129.28, 129.49, 142.52 (br), 145.24; δ_F (376 MHz, ppm down field from external CF_3CO_2H) −5.44 (3F), −34.68 (2F), −47.05 (2F), −47.41 (2F), −50.90 (2F); Found: *m*/*z* M^+ 412.0430, $C_{14}H_7F_{11}N_2$ requires 412.0433.

3-Perfluoropropyl-5-phenylpyrazole 15b. Colorless needles from hexane; mp 106.0–106.9 °C; NMR δ_H (500 MHz) 6.78 (s, 1H), 7.40–7.46 (m, 3H), 7.56–7.60 (m, 2H), 11.91 (brs, 1H); δ_C (125.7 MHz) 102.71, 125.61, 127.91, 129.27, 129.49, 142.29 (br), 145.24; δ_F (376 MHz, ppm down field from external CF_3CO_2H) −4.82 (3F), −35.64 (2F), −51.70 (2F); Found: *m*/*z* M^+ 312.0461, $C_{12}H_7F_7N_2$ requires 312.0497.

3-Perfluorononyl-5-phenylpyrazole 15c. δ_H (500 MHz) 6.80 (s, 1H), 7.42–7.48 (m, 3H), 7.56–7.60 (m, 2H), 10.92 (brs, 1H); δ_C(125.7 MHz) 102.90, 125.67, 128.04, 129.36, 129.54, 142.71 (br), 145.17; δ_F (376 MHz, ppm down field from external CF_3CO_2H) −5.40 (3F), −34.63 (2F), −45.99 (2F), −46.49 (6F), −47.17 (2F), −47.35 (2F), −50.76 (2F); Found: *m*/*z* M^+ 612.0319, $C_{18}H_7F_{19}N_2$ requires 612.0332.

5-(*p*-Chlorophenyl)-3-perfluoropentylpyrazole 15d. Colorless needles from hexane; mp 131.6–132.3 °C; NMR δ_H (500 MHz) 6.82 (s, 1H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 8.7 Hz, 2H), the NH proton did not appear in $CDCl_3$; δ_C (100.4 MHz) 103.22, 126.64, 126.97, 129.60, 135.62, 142.30 (br), 144.56; δ_F (376 MHz, ppm down field from external CF_3CO_2H) −5.43 (3F), −34.66 (2F), −47.03 (2F), −47.41 (2F), −50.88 (2F); Found: *m*/*z* M^+ 446.0036, $C_{14}H_6ClF_{11}N_2$ requires 446.0043.

3-Perfluoropentyl-5-(*p*-tolyl)pyrazole 15e. Colorless needles from hexane; mp 159.7–160.3 °C; NMR δ_H (400 MHz, $CDCl_3$) 2.53 (s, 3H), 6.78 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H) 11.63 (brs, 1H); δ_C (100.4 MHz) 21.27, 102.44, 125.18, 125.52, 129.95, 139.57, 142.54 (t, J_{CCF} = 29 Hz), 145.25; δ_F (376 MHz, ppm down field from external CF_3CO_2H) −5.45 (3F), −34.65 (2F), −47.04 (2F), −47.38 (2F), −50.90 (2F); Found: *m*/*z* M^+ 426.0580, $C_{15}H_9F_{11}N_2$ requires 426.0590.

5-Perfluoropropyl-7-phenyl-2,3-dihydro-1*H*-1,4-diazepine 17a. One-pot synthesis of dihydrodiazepines **17** was carried out as described above for the preparation of pyrazole. Yellow oil; NMR δ_H (500 MHz) 3.39 (brs, 2H), 4.06 (brs, 2H), 5.29 (s, 1H), 7.38–7.42 (m, 2H), 7.42–7.46 (m, 1H), 7.48–7.51 (m, 2H), the NH proton did not appear; δ_C (125.7 MHz) 48.79, 57.13, 88.62, 127.17, 128.84, 130.37, 138.47, 156.51 (t, J_{CCF} = 23 Hz), 157.09; δ_F (376 MHz, ppm down field from external CF_3CO_2H) −4.91 (3F), −39.83 (2F), −50.60 (2F); Found: *m*/*z* M^+ 340.0796, $C_{14}H_{11}F_7N_2$ requires 340.0800.

5-Perfluoropentyl-7-phenyl-2,3-dihydro-1*H*-1,4-diazepine 17b. Yellow oil; NMR δ_H (500 MH) 3.46 (brs, 2H), 4.07 (brs, 2H), 5.31 (s, 1H), 5.61 (brs, 1H), 7.38–7.42 (m, 2H), 7.43–7.47 (m, 1H), 7.48–7.51 (m, 2H); δ_C (125.7 MHz) 48.69, 57.42, 88.59, 127.19, 128.84, 130.34, 138.51, 156.79, 157.08 (br, t); δ_F (376 MHz, ppm down field from external CF_3CO_2H) −5.46 (3F), −38.79 (2F), −46.16 (2F), −46.89 (2F), −50.81 (2F); Found: *m*/*z* M^+ 440.0755, $C_{16}H_{11}F_{11}N_2$ requires 440.0746.

5-Perfluorononyl-7-phenyl-2,3-dihydro-1*H*-1,4-diazepine 17c. Yellow oil; NMR δ_H (400 MHz) 3.51 (brs, 2H), 4.11 (brs, 2H), 5.33 (s, 1H), 7.39–7.48 (m, 3H), 7.49–7.52 (m, 2H), the NH proton did not appear; δ_C (100.4 MHz) 48.86, 57.07, 88.85, 127.10, 128.81, 130.33, 138.46, 156.59 (t, J_{CCF} = 21 Hz), 157.08 (br, t); δ_F (376 MHz, ppm down field from external CF_3CO_2H) −5.43 (3F), −38.67 (2F), −45.87(4F), −46.36 (4F), −46.54 (2F), −47.34 (2F), −50.76 (2F); Found: *m*/*z* M^+ 640.0646, $C_{20}H_{11}F_{19}N_2$ requires 640.0619.

4-Perfluoropropyl-6-phenylpyrimidine 18a. One-pot synthesis of pyrimidines **18** was also carried out as described above for the preparation of pyrazole. Yellow oil; NMR δ_H (400 MHz) 7.54–7.59 (m, 3H), 8.05 (s, 1H), 8.14–8.17 (m, 2H), 9.42 (s, 1H); δ_C (125.7 MHz) 114.38, 127.48, 129.29, 132.15, 135.35, 156.51 (t, J_{CCF} = 26 Hz), 159.25, 166.31; δ_F (376 MHz, ppm down field from external CF_3CO_2H) −4.79 (3F), −41.57 (2F), −50,86 (2F);

Found: m/z M^+ 324.0477, $C_{13}H_7F_7N_2$ requires 324.0497.

4-Perfluoropentyl-6-phenylpyrimidine 18b. Yellow oil; NMR δ_H (400 MHz) 7.54–7.60 (m, 3H), 8.05 (s, 1H), 8.16–7.19 (m, 2H), 9.42 (s, 1H); δ_C (125.7 MHz) 114.43, 127.47, 129.29, 132.15, 135.34, 156.44 (t, $J_{CCF} = 26$ Hz), 159.20, 166.29; δ_F (376 MHz, ppm down field from external CF_3CO_2H) −5.42 (3F), −40.57 (2F), −46.49 (2F), −46.82 (2F), −50,79 (2F); Found: m/z M^+ 424.0417, $C_{15}H_7F_{11}N_2$ requires 424.0433.

4-Perfluorononyl-6-phenylpyrimidine18c. Yellow oil; NMR δ_H (400 MHz) 7.56–7.60 (m, 3H), 8.06 (s, 1H), 8.16–8.19 (m, 2H), 9.42 (s, 1H); δ_C (125.7 MHz) 114.46, 127.47, 129.31, 132.16, 135.34, 156.45 (t, $J_{CCF} = 26$ Hz), 159.19, 166.30; δ_F (376 MHz, ppm down field from external CF_3CO_2H) −5.40 (3F), −40.52 (2F), −45.79 (2F), −46.35 (8F), −47.34 (2F), −50,79 (2F); Found: m/z M^+ 624.0298, $C_{19}H_7F_{19}N_2$ requires 624.0306.

Typical Procedure for the One-Pot Synthesis of Pyrazolium Salt 16. A solution of perfluoroalkyl iodide (0.40 mmol), α-chlorostyrene (1.20 mmol), and $(Bu_3Sn)_2$ (0.44 mmol) in 3 mL of benzene was irradiated using a metal halide lamp in a Pyrex tube under an O_2 atmosphere for 5 h. After removal of the benzene from the photochemical reaction mixture, the residue was dissolved in MeOH and perhydropyridazine was added to the solution. The resulting solution was stirred at room temperature for 5 h. After removal of MeOH, the residue was dissolved in CH_3CN. The solution was washed with hexane to remove the tin compounds. After evaporation, gel permeation chromatography of the residue gave the salt **16**. The crude **16** was further purified by recrystallization from hexane–dichloromethane.

3-Perfluoropropyl-5-phenyl-1,2-tetramethylenepyrazolium Iodide 16a. Colorless plates; mp 143.7–144.9 °C; NMR δ_H (400 MHz) 2.42 (m, 2H), 2.52 (m, 2H), 4.83–4.88 (m, 4H), 7.05 (s, 1H), 7.55–7.63 (m, 3H), 7.84–7.87 (m, 2H); δ_C (100.4 MHz) 18.90, 18.90, 50.51, 51.01, 110.72, 1234.00, 129.56, 129.94, 132.10, 134.98 (t, $J_{CCF} = 31$ Hz), 149.71; δ_F (376 MHz, ppm down field from external CF_3CO_2H) −4.18 (3F), −33.86 (2F), −49.12 (2F); FAB-MS m/z 367 ($M^+ - 127$); Calcd for $C_{16}H_{14}F_7IN_2$: C, 38.89; H, 2.86; N, 5.67%; Found: C, 38.76; H, 3.00; N, 5.46%.

3-Perfluoropentyl-5-phenyl-1,2-tetramethylenepyrazolium Iodide 16b. Colorless plates; mp 163.7–164.5 °C; NMR δ_H (400 MHz) 2.42 (m, 2H), 2.53 (m, 2H), 4.89–4.95 (m, 4H), 7.08 (s, 1H), 7.58–7.64 (m, 3H), 7.78–7.81 (m, 2H); δ_C (100.4 MHz) 18.88, 18.92, 50.46, 50.95, 110.78, 123.88, 129.62, 129.87, 132.19, 135.30 (t, $J_{CCF} = 28$ Hz), 149.81; δ_F (376 MHz, ppm down field from external CF_3CO_2H) −5.22 (3F), −33.08 (2F), −44.97 (2F), −46.68 (2F), −50.63 (2F); FAB-MS m/z 594 (M^+), 468 ($M^+ - 126$); Calcd for $C_{18}H_{14}F_{11}IN_2$: C, 36.38; H, 2.37; N, 4.71%; Found: C, 36.41; H, 2.34; N, 4.72%.

3-Perfluorononyl-5-phenyl-1,2-tetramethylenepyrazolium Iodide 16c. NMR δ_H (400 MHz) 2.42 (m, 2H), 2.52 (m, 2H), 4.86–4.89 (m, 4H), 7.06 (s, 1H), 7.56–7.62 (m, 3H), 7.78–7.81 (m, 2H); δ_C (100.4 MHz) 18.83, 18.86, 50.42, 50.92, 110.73, 123.92, 129.54, 129.85, 132.07, 135.15 (t, $J_{CCF} = 28$ Hz), 149.67; δ_F (376 MHz, ppm down field from external CF_3CO_2H) −5.83 (3F), −33.12 (2F), −45.03 (2F), −46.58 (4F), −47.05 (4F), −47.47 (2F), −50.95 (2F); FAB-MS m/z 667 ($M^+ - 127$).

Preparation of Isoxazoles 19 and 22 from 2a. To a stirred solution of hydroxylamine hydrochloride (0.6 mmol) and Et_3N (6.5 mmol) in CH_2Cl_2 (3 mL) was added **2a** (0.5 mmol) in 2 mL of CH_2Cl_2 at room temperature. The reaction mixture was stirred at room temperature for 5 h. After the evaporation of CH_2Cl_2 and Et_3N, column chromatography of the residue on silica gel using hexane–benzene as an eluent gave products **19** and **20**.

5-Perfluoropentyl-3-phenyliosoxazole 19. Colorless needles from pentane; mp 58.5–60.4 °C; NMR δ_H (400 MHz) 7.07 (s, 1H), 7.49–7.52 (m, 3H), 7.81–7.84 (m, 2H); δ_C (100.4 MHz) 105.45, 126.07, 126.97, 129.19, 130.95, 158.83 (t, $J_{CCF} = 32$ Hz), 162.74; δ_F (376 MHz, ppm down field from external CF_3CO_2H) −5.38 (3F), −36.43 (2F), −47.26 (4F), −50.84 (2F); Found: m/z M^+ 413.0287, $C_{14}H_6F_{11}NO$ requires 413.0274.

3-Perfluoropentyl-5-phenyl-2-isoxazolin-5-ol 20. Colorless needles; mp 94.4–95.8 °C. ^1H and ^{19}F NMR indicated that **20** was at equilibrium with **21** in $CDCl_3$; NMR δ_H of **20** (400 MHz) 3.28 (d, $J = 18.3$ Hz, 1H), 3.38 (s, 1H), 3.48 (d, $J = 18.3$ Hz, 1H), 7.42–7.46 (m, 3H), 7.53–7.57 (m, 2H) and δ_H of **21** 4.20 (s, 2H), 7.50–7.54 (m, 2H), 7.61–7.65 (m, 1H), 7.97–8.01 (m, 2H), 8.36 (s, 1H); δ_F of **20** (376 MHz) −5.38 (3F), −36.32 (d, $J = 290$ Hz, 1F), −37.53 (d, $J = 290$ Hz, 1F), −46.85 (2F), −47.04 (2F), −50.81 (2F) and δ_F of **21** −5.38 (3F), 37.84 (2F), −46.17 (2F), −46.74 (2F), −50.81 (2F).

3-Perfluoropentyl-5-phenyliosoxazole 22. The product **20** was dissolved in benzene, and the solution was heated in the presence of a catalytic amount of p-TsOH for 2 h. The benzene solution was washed with 5% aqueous $NaHCO_3$ and then with brine. After evaporation of benzene, **22** was obtained. Colorless needles from pentane; mp 58.1–58.5 °C; NMR δ_H (500 MHz) 6.76 (s, 1H), 7.51–7.56 (m, 3H), 7.81–7.84 (m, 2H); δ_C (100.4 MHz) 98.02, 126.05, 126.10, 129.30, 131.35, 155.37 (t, J_{CCF} 32 Hz), 172.51; δ_F (376 MHz, ppm down field from external CF_3CO_2H) −5.26 (3F), −35.93 (2F), −46.79 (2F), −47.18, −50.72 (2F); Found: m/z M^+ 413.0281, $C_{14}H_6F_{11}NO$ requires 413.0274.

Selective Synthesis of Isoxazoles 19 and 20 from 14. A solution of **14** (0.13 mmol) and hydroxylamine hydrochloride (0.75 mmol) in MeOH (4 mL) in the presence of Et_3N (6.5 mmol) was stirred at room temperature for 5 h. After the removal of MeOH and Et_3N, the residue was dissolved in benzene and the solution was heated under reflux in the presence of a catalytic amount of p-TsOH for 2 h. The reaction mixture was washed with 5% aqueous $NaHCO_3$ and then with brine. After the evaporation of benzene, the residue was purified by column chromatography on silica gel to afford **22** in 79% yield.

A solution of **14** (0.13 mmol) and hydroxylamine hydrochloride (0.75 mmol) in MeOH (4 mL) in the presence of NaOH pellet (2.3 mmol) was heated with stirring under reflux for 5 h. After removal of MeOH, the organic products were extracted with ether (10 mL) and the ether solution was washed with 10 mL of water. After the evaporation of ether, the residue was purified by column chromatography on silica gel to afford **19**.

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