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Absolute Rate Constants for Radical Additions to Alkenes in Solution. The Synergistic Effect of Perfluorination on the Reactivities of *n*-Alkyl Radicals[1]

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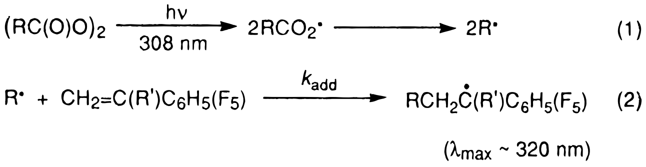
Laser flash photolysis has been used to determine the absolute rate constants for addition of several partially fluorinated *n*-alkyl radicals to three styrenes at 25 °C in Freon 113. Fluorination at the γ-position ($RCF_2CH_2CH_2^\bullet$) gives radicals with essentially the same reactivity as non-fluorinated *n*-alkyls. The $RCH_2CF_2CH_2^\bullet$ and $RCH_2CH_2CHF^\bullet$ radicals are both about three times as reactive as $RCF_2CH_2CH_2^\bullet$, but the $RCH_2CH_2CF_2^\bullet$ radical is ca. five to six times rather than ca. three times as reactive as $RCH_2CH_2CHF^\bullet$. Similarly, the perfluorinated radical $CF_3CF_2CF_2^\bullet$ is much more reactive than would be expected on the basis of the reactivities of the $RCH_2CF_2CH_2^\bullet$ and $RCH_2CH_2CF_2^\bullet$ radicals. Thus, perfluorinated *n*-alkyl radicals are very considerably more reactive than would be predicted from the individual effects of α-, β-, and γ-fluorination.

In some recent kinetic studies using laser flash photolysis (LFP) we demonstrated that perfluoro-*n*-alkyl radicals add to alkenes much more rapidly than *n*-alkyl radicals.[3,4] In the present paper we describe our experiments with partially-fluorinated *n*-alkyl radicals which are increasingly used in organic syntheses.[5] These kinetic measurements were made with the expectation that the enhanced reactivities of the perfluoro-*n*-alkyl radicals could be attributed to some linear combination of the individual effects of fluorine atoms on the α-carbon (the radical center), the β-carbon, and the γ-carbon atoms. However, to our surprise, we have discovered that the effect on radical reactivity of perfluorination is considerably greater than the sum of its parts.

Results

Radicals were generated "instantaneously" by 308 nm LFP of the parent diacyl peroxide (ca. 0.16 M, generally in $CFCl_2CF_2Cl$ at room temperature) and their addition to styrene, α-methylstyrene, and pentafluorostyrene were monitored directly *via* observation of the pseudo-first-order growth of the absorption at ca. 320 nm due to formation of the benzylic radical, as previously described,[3,4] see Scheme 1. The rate constants for the addition reaction were calculated from experimental growth curves measured over a range of styrene concentrations, see Table 1. For each alkyl radical the range of concentrations used for each styrene was selected in such a way that k_{add} $[CH_2{=}C(R')C_6H_5(F_5)]$ varied typically from a low of ca. 1×10^5 s^{-1} to a high of ca. 1×10^6 s^{-1}.

Scheme 1



$$(RC(O)O)_2 \xrightarrow[308\ nm]{h\nu} 2RCO_2^\bullet \longrightarrow 2R^\bullet \quad (1)$$

$$R^\bullet + CH_2{=}C(R')C_6H_5(F_5) \xrightarrow{k_{add}} RCH_2\dot{C}(R')C_6H_5(F_5) \quad (2)$$

$$(\lambda_{max} \sim 320\ nm)$$

$$k_{exptl}(320\ nm) = k_o + k_{add}\ [CH_2{=}C(R')C_6H_5(F_5)] \qquad I$$

In equation I, k_o represents the intercept in the plot of k_{exptl} vs $[CH_2{=}C(R')C_6H_5(F_5)]$; typically k_o was ca. 1×10^4 s^{-1}.

Discussion

The LFP technique is unsuited to the measurement of bimolecular rate constants for radical/molecule reactions that are smaller than 10^5 M^{-1} s^{-1}, and it is not particularly reliable for rate constants lying in the range 10^5–10^6 M^{-1} s^{-1}. With this in mind, it is clear that $RCF_2CH_2CH_2^\bullet$ radicals have *roughly* the same reactivities toward styrene and pentafluorostyrene as do non-fluorinated primary alkyl radicals (see Table 1).[6] That is, the γ-fluorine atoms are essentially without effect on radical reactivity. In contrast, there are dramatic and nonadditive rate enhancements when the hydrogens at the β- and α-positions are (progressively) substituted by fluorine. Thus, $RCH_2CF_2CH_2^\bullet$ and $RCH_2CH_2CHF^\bullet$ are both ca. three times as reactive as $RCF_2CH_2CH_2^\bullet$. However, the $RCH_2CH_2CF_2^\bullet$ radical is not ca. three times as reactive as $RCH_2CH_2CHF^\bullet$, but is, instead, about five to six times as reactive. That is, the second α-fluorine atom produces an extra (synergistic) enhancement in the radical's reactivity of roughly a factor of two. Furthermore, if we continue this series of α-substitutions all the way to the $CF_3^\bullet$ radical[7] we see that this trend of

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[6] The "modified" (see footnote b to Table 1) rate constant for addition of a non-fluorinated *n*-alkyl radical to α-methylstyrene is probably about a factor of 5 lower than the true value. Certainly, it seems very improbable that addition to this substrate could be slower than addition to styrene.

[7] This extension of the α-fluoroalkyl radical series can be justified by the fact that $CH_2F^\bullet$ and $CHF_2^\bullet$ have reactivities roughly comparable to those of $RCH_2CH_2CHF^\bullet$ and $RCH_2CH_2CF_2^\bullet$, respectively.[8]

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Table 1. Absolute Rate Constants (and Relative Rate Constants in Parentheses) for Reactions of Alkyl and Fluorine-Substituted Alkyl Radicals with Three Styrenes in Freon 113 at 298 ± 2 K, as Measured by LFP

	$k_{add}/10^6\ M^{-1}\ s^{-1}$ [a]		
radical	$C_6H_5CH{=}CH_2$	$C_6H_5C(CH_3){=}CH_2$	$C_6F_5CH{=}CH_2$
$CH_3CH_2CH_2CH_2CH_2^{\bullet}$	0.12[b] (0.92)	0.06[b,c] (0.18)	0.31 ± 0.08 (1.35)
$CF_3(CF_2)_2CF_2CH_2CH_2^{\bullet}$	0.13 ± 0.02 (1)	0.34 ± 0.09 (1)	0.23 ± 0.03 (1)
$CH_3CH_2CH_2CF_2CH_2^{\bullet}$	0.52 ± 0.18 (4.0)	0.98 ± 0.09 (2.9)	0.39 ± 0.09 (1.7)
$CH_3CH_2CH_2CH_2CHF^{\bullet}$	0.46 ± 0.05 (3.5)	*d*	0.70 ± 0.13 (3.0)
$CH_3CH_2CH_2CH_2CF_2^{\bullet}$	2.7 ± 0.5 (21)	3.3 ± 0.5 (9.7)	3.1 ± 0.3 (14)
$CF_3^{\bullet}$ [e]	53 ± 6 (410)	87 ± 8 (260)	26 ± 2 (110)
$CF_3CF_2CF_2^{\bullet}$	43 ± 1[f] (333)	78 ± 8[f] (230)	13 ± 1[f] (57)

[a] Errors correspond to 2σ but include only random errors. [b] From Citterio, A.; Arnoldi, A.; Minisci, F. *J. Org. Chem.* **1979**, *44*, 2674−2682, as modified for temperature and other factors in Table III of Johnston, L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1984**, *106*, 4877−4881. [c] Probably too low by a factor of ~5, see footnote 6. [d] Not measured. [e] This radical was generated by LFP of CF_3I. [f] Data are from ref 4.

unexpectedly large rate enhancements continues with the $CF_3^{\bullet}$ radical being from 8 to 27 times as reactive as the $RCH_2CH_2CF_2^{\bullet}$ radical. Equally interesting is the fact that the perfluorinated radical, $CF_3CF_2CF_2^{\bullet}$, which is roughly 75% as reactive as the $CF_3^{\bullet}$ radical, is about 15 times (range 4−24) as reactive as $RCH_2CH_2CF_2^{\bullet}$ whereas the rate enhancement expected on the basis of $RCF_2CH_2CH_2^{\bullet}$ and $RCH_2CF_2CH_2^{\bullet}$ would lead one to expect only a factor of 3. Thus, perfluorinated *n*-alkyl radicals are very considerably more reactive than would be predicted from the individual effects of α-, β-, and γ-fluorination.

The rather similar reactivities of $RCH_2CH_2^{\bullet}$ and $RCF_2CH_2^{\bullet}$ radicals are consistent with the fact that the ESR parameters for these two types of radical are very similar.[9,10] The increase in reactivities along the series $RCH_2CH_2^{\bullet} < RCH_2CHF^{\bullet} < RCH_2CF_2^{\bullet} < CF_3^{\bullet}$ is also consistent with the ESR parameters of these radicals which indicate a monotonic change in the configuration at the radical center along this series from the planar $RCH_2CH_2^{\bullet}$ radical to the approximately tetrahedral $CF_3^{\bullet}$ radical.[9,11] Undoubtedly, increasing the pyramidalization at the radical center will tend to increase the rate of a radical's addition to an alkene.[12] Indeed, recent calculations indicate that substantial bending occurs in the transition state for the addition of (planar) alkyl radicals to alkenes.[15] The energy required to bend the methyl and *tert*-butyl radicals to the same extent as in their respective transition state structures for addition to ethylene was calculated to be 1.6 and 1.5 kcal/mol, respectively.[15] Since one or two α-fluorine substituents give rise to alkyl radicals with a distinctly pyramidal configuration, these σ-radicals would be expected to have an inherent energetic advantage in addition reactions over planar alkyl radicals (including β- and γ-fluorine substituted *n*-alkyl radicals).

The ESR parameters for perfluoro-*n*-alkyl radicals[9,16] would seem to imply that their configuration at the radical center is more similar to that of $CHF_2^{\bullet}$ and $RCH_2CF_2^{\bullet}$ radicals than to the $CF_3^{\bullet}$ radical.[11] This suggests that both α,α-difluoro-*n*-alkyl and perfluoro-*n*-alkyl radicals are sufficiently nonplanar at their radical centers that little or no further bending is required in the transition states for their respective additions to alkenes.

Thermodynamic factors probably also play some role in the enhanced reactivity of α-fluoro and α,α-difluoroalkyl radicals relative to their non-fluorinated analogues since the $CF_3{-}CH_3$ bond dissociation energy (~101 kcal/mol)[17] would appear to be about 11 kcal/mol greater than that for $CH_3{-}CH_3$ (~90 kcal/mol).[18] The C−C bond dissociation energies for monofluoroethane, $CH_2F{-}CH_3$, viz.,[19] ~93 kcal/mol, and α,α-difluoroethane, $CHF_2{-}CH_3$, viz.,[19] ~97 kcal/mol, lie between these two extremes. Nevertheless, it should be noted that radical additions to double bonds involve early transition states, and therefore the overall enthalpies of reaction will be relatively unimportant. Indeed, as we have pointed out previously[3,4] the dominant factor giving rise to the high reactivities of perfluoro-*n*-alkyl radicals in their additions to alkenes, particularly to electron-rich alkenes,[3,4] is the high electrophilicities of these very electron-deficient radicals. That is, charge transfer interactions, e.g.,

$$[(CF_3CF_2CF_2^{\bullet})^{\delta-}\ (\text{alkene})^{\delta+}]^{\ddagger}$$

stabilize an early transition state and lower both the enthalpic and entropic[20] barriers to reaction, and, consequently, the reaction rate is increased.[21] Consistent

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(8) For example, in acetonitrile $k_{add}\ (CH_2F^{\bullet} + C_6F_5CH{=}CH_2) = (0.35 \pm 0.04) \times 10^6\ M^{-1}\ s^{-1}$, $k_{add}\ (CHF_2^{\bullet} + C_6H_5CH{=}CH_2) = (4.1 \pm 0.4) \times 10^6\ M^{-1}\ s^{-1}$ and $k_{add}\ (CHF_2^{\bullet} + C_6F_5CH{=}CH_2) = (5.5 \pm 0.7) \times 10^6\ M^{-1}\ s^{-1}$ (cf., Table 1).

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(10) E.g.,[9] $CH_3CH_2^{\bullet}$, $a\ (2H\alpha) = -22.2$ G, $a\ (^{13}C\alpha) = +39.1$ G, $g = 2.0026$; $CH_3CH_2CH_2^{\bullet}$, $a\ (2H\alpha) = -22.1$ G, $g = 2.0026$; $CF_3CH_2^{\bullet}$, $a\ (2H\alpha) = -23.8$ G, $g = 2.0023$; $CF_3CF_2CH_2^{\bullet}$, $a\ (2H\alpha) = -22$ G.

(11) E.g.,[9] $RCH_2CH_2^{\bullet}$;[10] $CH_2F^{\bullet}$, $a\ (2H\alpha) = -21.1$ G, $a\ (F\alpha) = +64.3$ G, $a\ (^{13}C\alpha) = +54.8$ G, $g = 2.0045$; $CF_3OCH_2CHF^{\bullet}$, $a\ (H\alpha) = -21.4$ G, $a\ (F\alpha) = +63.5$ G; $CHF_2^{\bullet}$, $a\ (H\alpha) = +22.2$ G, $a\ (2F\alpha) = +84.2$ G, $a\ (^{13}C\alpha) = +148.8$ G, $g = 2.0041$; $CF_3OCH_2CF_2^{\bullet}$, $a\ (2F\alpha) = +90.6$ G; $CF_3^{\bullet}$, $a\ (3F\alpha) = +142.4$ G, $a\ (^{13}C\alpha) = +271.6$ G, $g = 2.0031$.

(12) The greater reactivity of "bent" σ-radicals relative to planar π-radials has been noted earlier in studies on aryl radicals,[13] and the influence of pyramidality on radical reactivities has been previously suggested in a study of α-hydroxyalkyl radicals.[14]

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(16) E.g.,[9] $CF_3CF_2^{\bullet}$, $a\ (2F\alpha) = 87.6$ G, $g = 2.0037$; $CF_3CF_2CF_2^{\bullet}$, $a\ (2F\alpha) = 86.2$ G, $g = 2.0039$.

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(21) As would be expected for a reaction with a polar transition state the addition of perfluoroalkyl radicals to alkenes are faster in CH_3CN than in Freon 113 with this solvent effect being greater for the more electron-rich alkenes. For example, the rate acceleration in CH_3CN relative to the Freon solvent for addition to styrene by $CF_3^{\bullet}$ and $CF_3CF_2CF_2^{\bullet}$ is about a factor of 3, but for the addition of these two radicals to pentafluorostyrene the rate acceleration is only ca. 50%. For

with this concept is the fact (see Table 1) that the rates of addition of $CF_3CF_2CF_2^{\bullet}$ to the three styrenes increase as the ionization potentials of the styrenes decrease,[4] viz., $C_6F_5CH{=}CH_2$, IP = 9.20 eV; $C_6H_5CH{=}CH_2$, IP = 8.43 eV; $C_6H_5C(CH_3){=}CH_2$, IP = 8.19 eV. The same trend occurs with the $CF_3^{\bullet}$ radical. In contrast, the $CH_3(CH_2)_3CF_2^{\bullet}$ radical adds to these three alkenes at the same rate (within experimental error). Thus, while $CF_3CF_2CF_2^{\bullet}$ and $CF_3^{\bullet}$ are undoubtedly electrophilic, the $CH_3(CH_2)_3CF_2^{\bullet}$ radical exhibits neither electrophilic nor nucleophilic characteristics.[25,26]

The fluorine atom and the CF_3 group appear to have rather similar electronegativities.[31] The polar contribution to stabilization of the transition states for addition of the $CF_3^{\bullet}$ and $CF_3CF_2CF_2^{\bullet}$ radicals to an alkene would therefore also be expected to be rather similar. Since the rates of addition of these two perfluorinated alkyl radicals to an alkene are similar (Table 1), we conclude that for both radicals the reaction rates are controlled principally by the extent to which polar effects stabilize the transition states.[32] Polar effects on transition state energies are very much less important for the partially fluorinated radicals studied in this work.

Experimental Section

General. ^1H, ^{13}C, and ^{19}F NMR spectra (300 MHz, 75 MHz and 282 MHz, respectively) were measured in $CDCl_3$ using TMS as internal standard for ^1H and ^{13}C, and $CFCl_3$ for ^{19}F.

Time-Resolved Laser Flash Photolysis. The apparatus and procedures have been described in detail elsewhere.[33] The rate constants for the reactions which resulted in the formation of the benzylic radicals (reaction 2) were determined from the experimental growth curves of the absorption at ca. 320 nm measured over a range of substrate concentrations, according to eq 1.

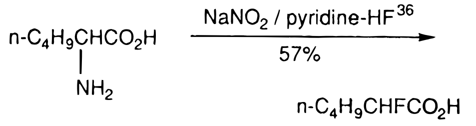
Preparation of Fluorodiacyl Peroxides. The various partially-fluorinated diacyl peroxides were prepared as solutions in Freon 113 from their respective acyl chlorides and purified using the procedure of Zhao *et al.* (reaction 3).[34]

$$\mathrm{RC(O)Cl} \xrightarrow[\text{F113, -5 °C}]{H_2O_2\text{ / NaOH}} (\mathrm{R{-}CO_2})_2 \qquad (3)$$

Determination of yield and concentration of the peroxides was accomplished by iodometry, and the solutions were preserved until needed at −78 °C. Yields of the diacyl peroxides were 79% for 2,2-difluorohexanoyl peroxide, 72% for 2-fluorohexanoyl peroxide, 82% for 3,3-difluorohexanoyl peroxide, and 96% for 4,4,5,5,6,6,7,7,7-nonafluoroheptanoyl peroxide.

Syntheses of Partially-Fluorinated Acyl Chlorides. The key fluorine-incorporating steps which were utilized in the syntheses of the various partially-fluorinated acid chloride precursors are shown below (reactions 4−8). Hydrolysis, if necessary, of each precursor, followed by treatment with thionyl chloride, provided the acyl chlorides.

$$n\text{-}C_4H_9COCO_2Me \xrightarrow[\text{-15 to 25 °C, 67\%}]{\text{DAST}^{35}} n\text{-}C_4H_9CF_2CO_2Me \qquad (4)$$



$$n\text{-}C_4H_9CH(NH_2)CO_2H \xrightarrow[57\%]{\text{NaNO}_2\text{ / pyridine-HF}^{36}} n\text{-}C_4H_9CHFCO_2H \qquad (5)$$

$$n\text{-}C_3H_7COCH_2CO_2Et \xrightarrow[82\%]{SF_4,CH_2Cl_2\ ^{37}} n\text{-}C_3H_7CF_2CH_2CO_2Et \qquad (6)$$

$$n\text{-}C_4F_9I + CH_2{=}CHCO_2Me \xrightarrow[\text{THF, 47\%}]{\text{Zn / Cobaloxime (III)}\ ^{38}} n\text{-}C_4F_9CH_2CH_2CO_2Me \qquad (7)$$

Methyl 2,2-difluorohexanoate was prepared in 67% yield by the reaction of methyl 2-oxohexanoate[39] with (diethylamido)sulfur trifluoride (DAST), according to the procedure of Middleton and Bingham:[35] bp 69 °C (15 mmHg); ^1H NMR δ 0.92 (3H, t, J = 7.3 Hz), 1.30−1.55 (4H, m), 1.70−2.20 (2H, m), 3.87 (3H, s); ^{19}F NMR δ −106.2 (t, J = 17.7 Hz); ^{13}C NMR δ 13.58 (s, CH_3), 22.13 (s, CH_2), 23.43 (t, J = 4.2 Hz, CH_2), 34.19 (t, J = 22.9 Hz, CH_2), 116.42 (t, J = 248.1 Hz, CF_2), 164.86 (t, J = 33.2 Hz, C=O), 53.10 (s, OCH_3); HRMS, calcd for $C_7H_{12}F_2O_2$ 166.0806; found 166.0799.

2,2-Difluorohexanoic Acid. Hydrolysis of the ester was accomplished by refluxing 10 g (0.06 mol) in a mixture of 20 mL 30% HCl and 20 mL acetic acid for 8 h. The mixture was extracted with 2 × 250 mL ether, followed by washing the ether layer with 10% $NaHCO_3$. The aqueous layer was

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comparison, Salikhov and Fischer[22] have found that the rate of addition of the nucleophilic *tert*-butyl radical to (electron-deficient) acrylonitrile (IP = 10.9 eV) is also somewhat accelerated in more polar solvents, e.g., k_{add} (CH_3CN)/k_{add} (c-C_6H_{12}) = 2.8. In connection with the foregoing, we note that solvent effects on the rates of radical additions to alkenes are never likely to be much larger than ca. 3−5.[23] Certainly, they will never be as dramatic as those recently reported for hydrogen atom abstractions from phenol and *tert*-butyl hydroperoxide by the cumyloxyl radical.[24]

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(25) It has, in fact, even been proposed on the basis of intramolecular cyclization studies that $RCH_2C(CO_2Me)_2CF_2^{\bullet}$ radicals (R = CH_2-$CH{=}CH_2$ and related groups) preferentially exhibit nucleophilic character, see: Buttle, L. A.; Motherwell, W. B. *Tetrahedron Lett.* **1994**, *35*, 3995−3998. For other studies on the intramolecular cyclization of α,α-difluoroalkenyl radicals, see: ref 5a.

(26) A measure of the ‘philicity of the prototypical non-fluorinated and fluorinated alkyl radicals, $CH_3^{\bullet}$, $CH_2F^{\bullet}$, $CHF_2^{\bullet}$, and $CF_3^{\bullet}$, is provided by their absolute electronegativities,[27] χ = (IP + EA)/2, which can be calculated to be 4.96, 4.73, 4.91, and 5.74, respectively, from experimental ionization potentials[28,29] and theoretically calculated electron affinities.[30] It is clear that one or two α-fluorine atoms do not make an alkyl radical more electrophilic than the corresponding non-fluorinated species and may even make them slightly more nucleophilic.

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carefully acidified with 18% HCl, then extracted with ether (2 × 200 mL), dried over $MgSO_4$, evaporated to remove ether and distilled to give 6.0 g (66%) of product: bp 83−85 °C (2.5 mm Hg); ^1H NMR δ 0.94 (3H, t, $J = 7.3$ Hz), 1.25−1.60 (4H, m), 2.05 (2H, m), 10.20 (s, OH); ^{19}F NMR δ −107.20 (t, $J =$ 16.0 Hz); ^{13}C NMR δ 13.58 (s, CH_3), 22.16 (s, CH_2), 23.37 (t, J = 4.1 Hz, CH_2), 34.0 (t, $J = 23.0$ Hz, CH_2), 116.2 (t, $J = 240.1$ Hz, CF_2), 169.2 (t, $J = 33.1$ Hz, C═O), Anal: Calcd. for $C_6H_{10}F_2O_2$; C, 47.37; H, 6.63; found; C, 47.16; H, 6.82.

2,2-Difluorohexanoyl chloride was prepared in 78% yield by treatment of the acid with $SOCl_2$ as described in Vogel:[40] bp 58−60 °C (40 mmHg); ^1H NMR δ 0.94 (3H, t, $J = 6.5$ Hz), 1.25−1.61 (4H, m), 2.11 (2H, m); ^{19}F NMR δ −102.41 (t, $J =$ 16.0 Hz); ^{13}C NMR δ 13.48 (s, CH_3), 22.1 (s, CH_2), 23.2 (t, $J =$ 3.7 Hz, CH_2), 33.3 (t, $J = 22.4$ Hz, CH_2), 117.2 (t, $J = 254.8$ Hz, CF_2), 164.0 (t, $J = 30.1$) Hz, C═O).

2-Fluorohexanoic acid was prepared by the methods of Olah *et al.*:[36] bp 81−83 °C (2.5 mmHg). The ^1H, ^{13}C, and ^{19}F NMR spectra were analogous to those of the ethyl ester reported by Thenappan and Burton.[41]

2-Fluorohexanoyl chloride was prepared in 58% yield by treatment of the acid with $SOCl_2$ as described by Vogel:[40] bp 65−67 °C (25 mmHg); ^1H NMR δ 0.94 (3H, t, $J = 7.4$ Hz), 1.3−1.6 (4H, m), 1.90−2.10 (2H, m), 5.04 (1H, dq, $J_{HF} = 49.3$ Hz, $J_{HH} = 4.6$ Hz); ^{19}F NMR δ −178.7 (dt, $J = 49.4$, 25.1 Hz).

Ethyl 3,3-difluorohexanoate was prepared by the method of Yagupolskii *et al.*[37] Into a 60 mL stainless steel autoclave was placed ethyl 3-oxohexanoate (15.8 g, 0.1 mol), SF_4 (13.0 g, 0.12 mol), and 5 mL of anhydrous HF. The mixture was shaken for 20 h at room temperature and then poured onto ice. The mixture was extracted with 100 mL ether and the ether layer subsequently washed with 10% Na_2CO_3 and water. After drying with $MgSO_4$, the mixture was distilled to give 14.8 g (82%) of ethyl 3,3-difluorohexanoate: bp 88 °C (30 mmHg); ^1H NMR δ 0.98 (3H, t, $J = 7.3$ Hz), 1.53 (2H, m), 2.00 (2H, m) 2.89 (2H, t, $J = 14.6$ Hz), 4.19 (2H, q, $J = 7.1$ Hz), 1.28 (3H, t, $J = 7.1$ Hz); ^{19}F NMR δ −94.53 (p, $J = 15.7$ Hz); ^{13}C NMR δ 13.64 (s, CH_3), 13.90 (s, CH_3), 15.59 (t, $J = 4.9$ Hz, CH_2), 39.98 (t, $J = 24.0$ Hz, CH_2), 41.75 (t, $J = 28.6$ Hz, CH_2), 60.98 (s, CH_2), 122.14 (t, $J = 241$ Hz, CF_2), 166.98 (t, $J = 7.7$ Hz, C═O); HRMS calcd for $C_8H_{14}F_2O_2$ 180.0962; found 180.0948.

3,3-Difluorohexanoic acid was prepared in 79% yield by hydrolysis of the ester in a manner similar to that of 2,2-difluorohexanoic acid: bp 92−94 °C (2.0 mmHg); ^1H NMR δ 0.97 (3H, t, $J = 7.2$ Hz), 1.52 (2H, m), 1.95 (2H, m), 2.95 (2H, t, $J = 14.5$ Hz), 11.2 (s, OH); ^{19}F NMR δ −94.53 (p, $J = 15.6$ Hz); ^{13}C NMR δ 13.7 (s, CH_3), 15.6 (t, $J = 4.8$ Hz, CH_2), 38.1 (t, $J = 23.9$ Hz, CH_2), 41.6 (t, $J = 28.3$ Hz, CH_2), 121.9 (t, $J =$ 241.2 Hz, CF_2), 173.6 (t, $J = 7.6$ Hz, C═O). Anal. Calcd for $C_6H_{10}F_2O_2C$, 47.37; H, 6.63. Found: C, 47.20; H, 6.74.

3,3-Difluorohexanoyl chloride was prepared in 70% yield in the usual manner: bp 64−66 °C (28 mmHg); ^1H NMR δ 0.98 (3H, t, $J = 7.3$ Hz), 1.52 (2H, m), 1.97 (2H, m), 3.47 (2H, t, $J = 13.7$ Hz); ^{19}F NMR δ −95.48 (m); ^{13}C NMR δ 13.57 (s, CH_3), 15.51 (t, $J = 4.8$ Hz, CH_2), 37.83 (t, $J = 23.5$ Hz, CH_2), 52.5 (t, $J = 28.9$ Hz, CH_2), 120.7 (t, $J = 242.9$ Hz, CF_2), 167.1 (t, $J = 7.3$ Hz, C═O).

4,4,5,5,6,6,7,7,7-Nonafluoroheptanoic acid was prepared in 68% yield by hydrolysis of the ethyl ester in the same manner as for 2,2-difluorohexanoic acid: bp 90 °C (2 mmHg); ^1H NMR δ 2.39−2.69 (2H, m), 2.72 (2H, m); ^{19}F NMR δ −102.74 (3F, t, $J = 10.2$ Hz), −136.75 (2F, m), −146.20 (2F, m), −147.76 (2F, m); Anal. Calcd for $C_7H_5F_9O_2$; C, 28.78; H, 1.73. Found: C, 28.52; H, 1.90.

4,4,5,5,6,6,7,7,7-Nonafluoroheptanoyl chloride was prepared in 75% in the usual manner: bp 84−86 (74 mmHg); ^1H NMR δ 2.37−2.69 (2H, m), 3.24 (2H, t, $J = 7.1$ Hz); ^{19}F NMR δ −81.59 (3F, m), −124.90 (2F, m), −126.52 (2F, m), −115.2 (2F, m); ^{13}C NMR δ 26.49 (t, $J = 22.5$ Hz, CH_2), 38.1 (m, CH_2), 108−124 (m, CF_2's and CF_3) 171.9 (s, C═O).

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Supporting Information Available: Spectral data including ^1H, ^{13}C, and ^{19}F NMR spectra of the acyl chlorides (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet. See any current masthead page for ordering information and Internet access instructions.

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