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EXPERIMENTAL AND THEORETICAL STUDIES ON THE REACTIVITIES OF PARTIALLY AND FULLY FLUORINATED PRIMARY ALKYL RADICALS[ϕ]

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Abstract: Absolute rate constants for hydrogen abstraction from *n*-Bu_3SnH by a number of partially-fluorinated and fully fluorinated *n*-alkyl radicals have been measured. The C-H and C-C bond dissociation energies for a number of pertinent hydrofluorocarbons have been calculated by DFT. The rate data are compared with those for addition of the same radicals to styrene, and the reactivities of these radicals are discussed in terms of their electronegativies, their structure and the thermodynamics of their reactions.

In a series of recent publications we have reported absolute rate data for some alkene addition and hydrogen atom abstraction reactions of perfluoro-*n*-alkyl radicals.[1,2] These perfluoroalkyl radicals were found to be considerably more reactive than their non-fluorinated counterparts, and it was proposed that their enhanced reactivities were derived largely from stabilization of the transition states by polar effects which arise from the great electrophilicity of these radicals.[1,2] In addition, it was concluded that there was some enhancement of reactivity arising from the fact that the radical centers in perfluoro-*n*-alkyl radicals have a non-planar (i. e., pyramidal) geometry. Furthermore, there was some limited evidence to suggest that the reaction thermodynamics for the perfluorinated radicals would be more favorable (i.e., more exothermic) than the thermodynamics for the corresponding reactions of *n*-alkyl radicals.

Preliminary studies on the additions of some partially fluorinated *n*-alkyl radicals to alkenes showed relatively modest reactivity enhancements over their non-fluorinated counterparts.[3] The observed rate enhancements were attributed to combinations of the three factors mentioned above, although polar contributions to transition state stabilization appeared to be of less importance than for the perfluoro-*n*-alkyl radicals.

In the present paper, we extend our experimental studies on partially fluorinated *n*-alkyl radicals and have measured their absolute rate constants for hydrogen atom abstraction from tri-*n*-butyltin hydride. Knowledge of these particular rate constants (k_H) will prove invaluable in other ongoing investigations such as, e.g., determining the rate constants for cyclization of partially fluorinated 5-hexenyl radicals. In view of the paucity of bond dissociation energy (BDE) data for fluorine-containing hydrocarbons, we have also undertaken some density functional theory (DFT) calculations. The calculated C-H and C-C BDE's throw new light on the thermodynamics of hydrogen atom abstractions and alkene additions by partially and fully fluorinated *n*-alkyl radicals.

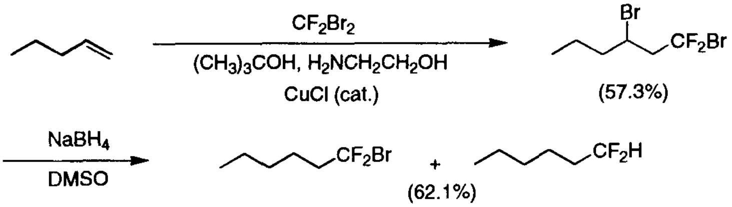
RESULTS

The following radicals have been employed in the current kinetic studies: $RCH_2CH_2CH_2^{\cdot}$ (*n*-alkyl), $R_FCF_2CH_2CH_2^{\cdot}$ (γ), $RCH_2CF_2CH_2^{\cdot}$ (β), $RCH_2CH_2CF_2^{\cdot}$ (α), $RCH_2CF_2CF_2^{\cdot}$ ($\alpha + \beta$), $CF_3CF_2^{\cdot}$ ($\alpha + \beta$), and $R_FCF_2CF_2CF_2^{\cdot}$ ($\alpha + \beta + \gamma$).

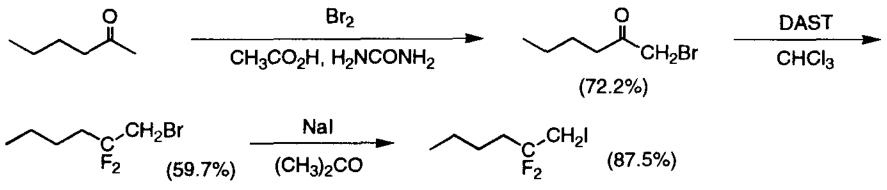
Radical Precursors

The above mentioned radicals were generated from their parent bromides or iodides. We thank Dr. Neal Brace and Halocarbons, Inc. for generous samples of $R_FCH_2CH_2I$ and 6-bromo-5,5,6,6-tetrafluoro-1-hexene, respectively. The CF_3CF_2I was purchased from PCR, Inc. The remaining compounds were either available from earlier work or were synthesized by the methods depicted in Schemes 1,2 and 3.

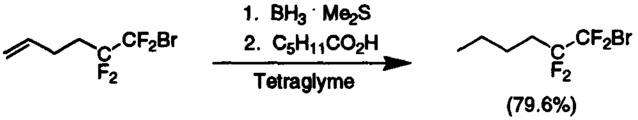
Scheme 1. Synthesis of 1-Bromo-1,1-difluorohexane



Scheme 2. Synthesis of 1-Iodo-2,2-difluorohexane



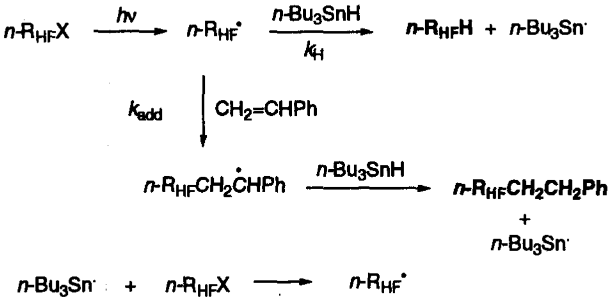
Scheme 3. Synthesis of 1-Bromo-1,1,2,2-tetrafluorohexane



Kinetic Studies

Rate constants for hydrogen atom abstraction from *n*-Bu$_3$SnH were obtained by a combination of competitive kinetics (i.e., relative rate constants) and nanosecond laser flash photolysis, LFP (i.e., absolute rate constants). The competitive experiments were carried out under free radical chain conditions and involved reaction of the radical *n*-R$_{HF}$· with known concentrations of tin hydride and styrene (see Scheme 4, where the two important products are shown in bold face). The ratios of the yields of *n*-R$_{HF}$H to *n*-R$_{HF}$CH$_2$CH$_2$Ph were determined directly by ^{19}F NMR analyses of the product mixtures,[4] and the rate constant ratios, k_H/k_{add}, were calculated via equation (i).[4]

Scheme 4



$$\frac{k_H}{k_{add}} = \frac{[n\text{-R}_{HF}\text{H}]}{[n\text{-R}_{HF}\text{CH}_2\text{CH}_2\text{Ph}]} \cdot \frac{[\text{CH}_2\text{=CHPh}]}{[n\text{-Bu}_3\text{SnH}]} \qquad \text{(i)}$$

Values of k_{add} were determined by 308 nm LFP of appropriate precursors of the *n*-R$_{HF}$· radicals in Freon 113 at room temperature by monitoring the pseudo-first-order growth of the absorption at ca. 320 nm due to the benzylic radical adduct,[1,3,5] see e.g., Scheme 5. These addition rate constants (some of which have been reported previously)[3] were calculated via equation (ii) and are summarized in Table 1 together with the abstraction rate constants, k_H, calculated from k_{add} and the k_H/k_{add} ratios determined in the competition experiments. (Note, in equation (ii), k_0 is simply the intercept of the plot of k_{exptl} vs [CH$_2$=CHPh], $k_0 \sim 1 \times 10^4$ s^{-1}.)

Scheme 5

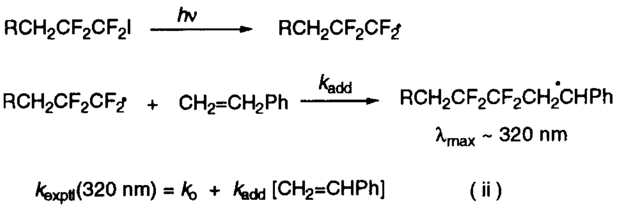


Table 1. Rate Constants for Hydrogen Abstraction from n-Bu_3SnH and for Addition to Styrene by Various Fluorinated Radicals at Room Temperature (25 ± 3 °C)

Radical	k_H[a]	k_{rel}	k_{add}	k_{rel}
$RCH_2CH_2^{\cdot}$	2.4 x 10^{6} (e)	(1)	1.2 x 10^{5} (f)	(1)
$RCH_2CF_2^{\cdot}$ [b], **2a**	9.1 (±1.7) x 10^{6}	3.8	2.7 x 10^{6} (g)	22.5
$RCF_2CH_2^{\cdot}$ [b], **2b**	1.4 (±0.5) x 10^{7}	5.8	5.2 x 10^{5} (g)	4.3
$R_fCH_2CH_2^{\cdot}$ [c], **2c**	2.1 (±0.3) x 10^{6}	0.9	1.3 x 10^{5} (g)	1.1
$RCF_2CF_2^{\cdot}$ [d], **2d**	9.2 (±0.8) x 10^{7}	38	2.0 (±0.1) x 10^{7}	167
n-$C_7F_{15}^{\cdot}$	2.0 x 10^{8} (h)	83	4.6 x 10^{7} (i)	383
$CF_3CF_2^{\cdot}$, **2e**	3.2 (±0.3) x 10^{8}	133	7.9 (±1.0) x 10^{7}	658

[a] Errors correspond to 2σ and have been propagated; [b] For k_H experiment, R = n-C_4H_9; for k_{add} expt, R = n-C_3H_7; [c] for k_H expt, R_f = n-C_6F_{13}; for k_{add} expt, R_f = n-C_4F_9; [d] for k_H expt, R = n-C_4H_9; for k_{add} expt, R = C_2H_5; [e] Chatgilialoglu, C.; Ingold, K.U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739-7742; [f] 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; [g] Ref. 3; [h] Ref. 2; [i] Ref. 1.

DFT Calculations

There are very few experimental C-C and C-H BDE's for fluorine-containing alkanes (see Tables 2 and 3, respectively). We therefore decided to calculate some C-C and C-H BDE's since these should, in a relative sense, reflect the thermochemistry of addition to styrene and hydrogen atom abstraction from n-Bu_3SnH, respectively, for the various radicals we have investigated.[6]

The results of our BDE calculations are summarized in Tables 2 and 3. In those cases where comparison is possible, the calculated BDE's are generally within 2-3 kcal/mol of the experimental values. Since the latter are, in fact, unlikely to be more reliable than ca ± 2 kcal/mol we believe that the calculated differences in C-C and C-H BDE's which are greater than ca. ± 1 kcal/mol probably reflect real differences in the BDE's.

Table 2. Calculated C-C Bond Dissociation Energies [B3LYP/6-31G(d)]

C-C Bond	BDE[a] (kcal/mol)	Exptl.
CH_3-CH_3	89.4	89.9±0.5[b,c]
CF_3-CH_3	99.6	101.2±1.1[b,d]
CH_3CH_2-CH_3	86.3	
CH_3CF_2-CH_3	91.4	
CF_3CH_2-CH_3	91.4	
CF_3CF_2-CH_3	95.5	
$CH_3CH_2CH_2$-CH_3	86.7	
$CH_3CH_2CF_2$-CH_3	91.6	
$CH_3CF_2CH_2$-CH_3	89.9	
$CH_3CF_2CF_2$-CH_3	95.4	
$CF_3CH_2CH_2$-CH_3	87.8	

[a] Reported as D_o(298.15 °K) in kcal/mol, using 0.9806 ZPE and a temperature correction of 4RT; [b] Ref. 8; [c] Ref. 9; [d] Ref. 10.

Table 3. Calculated C-H Bond Dissociation Energies [B3LYP/6-31G(d)]

C-H Bond	BDE[a] (kcal/mol)	Exptl.
CH_3CH_2-H	100.0	101.1±1[b,c]
CH_3CF_2-H	97.4	99.5±2.5[b,d]
CF_3CH_2-H	104.3	106.7±1[b,e]
CF_3CF_2-H	99.5	102.7±0.5[b,f]
$CH_3CH_2CH_2$-H	100.3	100.4±0.6[b]
$CH_3CH_2CF_2$-H	97.7	
$CH_3CF_2CH_2$-H	103.1	
$CH_3CF_2CF_2$-H	100.1	
$CF_3CH_2CH_2$-H	101.4	
$CF_3CF_2CH_2$-H	103.8	

[a] Reported as D_o(298.15 °K) in kcal/mol, using 0.9806 ZPE and a temperature correction of 2.5RT; [b] Ref. 8; [c] Ref. 11; [d] Ref. 12; [e] Ref. 13; [f] Ref. 14.

A knowledge of atomic charges is essential for one to be able to consider the impact of electrostatics upon bonding. Thus, using the B3LYP/6-31G(d) densities of the optimized structures, partial atomic charges were computed, based on both Mulliken populations and fits to the electrostatic potential at points selected according to the Merz-Kollman-Singh scheme.[15,16] Although the B3LYP/6-31G(d) values are listed here, it should be noted that the trends in the MKS-based atomic charges are also adhered to in the case of structures optimized at the SCF and MP2 levels with basis sets ranging from 6-31G(d) to 6-311++G(d,p), with charges of comparable magnitude generally being observed as well.[17]

Table 4. Atomic Charges in Select Hydrofluorocarbons, Based on the B3LYP/6-31G(d) density.

HFC	*method*	*F*	*α-C*	*β-C*	*α-H*	β-H
$C_{\alpha}H_3C_{\alpha}H_3$	MKS-ESP		-0.055		+0.018	
ethane	Mulliken		-0.433		+0.144	
$C_{\alpha}H_2F_2$	MKS-ESP	-0.200	+0.320		+0.041	
difluoromethane	Mulliken	-0.281	+0.299		+0.132	
$C_{\beta}H_3C_{\alpha}F_2H$	MKS-ESP	-0.228	+0.467	-0.386	+0.020	+0.110 (2H)
1,1-difluoroethane						+0.135 (1H)
	Mulliken	-0.291	+0.458	-0.502	+0.120	+0.165 (2H)
						+0.177 (1H)
$C_{\beta}H_3C_{\alpha}F_2C_{\beta}H_3$	MKS-ESP	-0.245	+0.631	-0.477		+0.133 (4H)
2,2-difluoropropane						+0.140 (2H)
	Mulliken	-0.307	+0.620	-0.497		+0.160 (4H)
						+0.175 (2H)

DISCUSSION

The trend of reactivities which is observed for hydrogen atom abstraction by fluorinated radicals is qualitatively similar to that for their addition to styrene. However, the absolute rates and the range of reactivities for each type of process can be seen to differ significantly. Thus, absolute rate constants for hydrogen atom abstraction from tin hydride by the radicals listed in Table 1 are greater by roughly an order of magnitude (range 3.4-27) than the absolute rate constants for addition of these same radicals to styrene. Indeed, the rate constants for hydrogen atom abstraction by the two perfluorinated radicals are within an order of magnitude of the diffusion-controlled limit. As a natural consequence, the range of fluorine-induced changes in reactivity is smaller for the hydrogen abstraction reactions (range 0.9 to 133) than for the addition reactions (range 1 to 658).

α,α-Difluoroalkyl radicals

If one considers the C-H bond-weakening effect of α,α-difluoro substitution, along with the demonstrated lack of impact of α,α-difluoro substitution on radical electrophilicity,[3] it is quite clear that the small (factor of 3.8) rate enhancement for hydrogen atom abstraction from *n*-Bu_3SnH by $RCH_2CH_2CF_2^{\cdot}$ relative to $RCH_2CH_2CH_2^{\cdot}$ must derive mainly from the pyramidal nature of the former radical.[18] The opposite effect of α,α-difluoro substitution on C-C BDE's helps to explain why there is a much more significant rate enhancement (factor of 22.5) for addition to styrene by $RCH_2CH_2CF_2^{\cdot}$ relative to $RCH_2CH_2CH_2^{\cdot}$.

β,β-Difluoroalkyl radicals

The β,β-difluorinated radicals are more interesting in that $RCH_2CF_2CH_2^{\cdot}$ is ca. 5 times as reactive as $RCH_2CH_2CH_2^{\cdot}$ in both hydrogen atom abstractions from *n*-Bu_3SnH and in additions to styrenes (Table 1). Since the $RCH_2CF_2CH_2^{\cdot}$ radicals are effectively planar,[18] their enhanced reactivities must derive from either polar or enthalpic factors. The latter is probably the more important. That is, the C-H bond in $CH_3CF_2CH_2$-H is calculated to be 2.8 kcal/mol stronger than that in $CH_3CH_2CH_2$-H (Table 3), and the C-C bond in $CH_3CF_2CH_2$-CH_3 is calculated to be 3.2 kcal/mol stronger than that in $CH_3CH_2CH_2$-CH_3 (See Table 2 and related discussion (*vide infra*)). The greater exothermicities of the $RCH_2CF_2CH_2^{\cdot}$ radical reactions appear to be quite sufficient to account for its very modest increase in reactivity relative to primary alkyl radicals.[19]

γ,γ-Difluoroalkyl radicals

The γ, γ-difluorinated radical $R_FCF_2CH_2CH_2^{\cdot}$ has essentially the same reactivity as a primary alkyl radical (Table 1) and essentially (within 1.1 kcal/mol) the same C-C and C-H BDE's as in the corresponding alkane (Tables 2 and 3).

Polyfluorinated radicals

All α,α-difluoroalkyl radicals are pyramidal, and furthermore, the degree of bending at the radical center would appear to be rather similar whether or not the radicals are more extensively fluorinated.[18] The enhanced reactivity of the $RCH_2CF_2CF_2^{\cdot}$, $R_FCF_2CF_2CF_2^{\cdot}$, and $CF_3CF_2^{\cdot}$ radicals relative to $RCH_2CH_2CF_2^{\cdot}$ radicals must therefore arise from either the greater electronegativity of these polyfluorinated radicals, or to more favorable thermodynamic factors, or both. The data in Tables 2 and 3 indicate that the trend in reactivities for these radicals correlates poorly with the thermodynamic driving force for the reactions in question. Thus, for the hydrogen atom abstraction, the rate constants (relative to that for the *n*-alkyl radical) for $RCH_2CH_2CF_2^{\cdot}$, $RCH_2CF_2CF_2^{\cdot}$, and $CF_3CF_2^{\cdot}$ are 3.8, 38 and 133, respectively, whereas the relevant C-H BDE's for the products which would be formed are 97.7, 100.1, and 99.5 kcal/mol, respectively. Similarly, the rate constants (relative to *n*-alkyl) for the addition to styrene of these same radicals are 22.5, 167 and 658, respectively, whereas the relevant C-C- BDE's are 91.6, 95.4 and 95.5 kcal/mol, respectively. Therefore, although there may be a small thermodynamically-induced rate enhancement for the abstraction and addition reactions on changing from the $-CH_2CF_2^{\cdot}$ moiety to the $-CF_2CF_2^{\cdot}$ and $CF_3CF_2^{\cdot}$ moieties, it cannot fully account for the observed changes in rate constants. We therefore conclude that polar effects arising from the greater electronegativities of $RCH_2CF_2CF_2^{\cdot}$, $R_FCF_2CF_2CF_2^{\cdot}$ and $CF_3CF_2^{\cdot}$ versus that of $RCH_2CH_2CF_2^{\cdot}$ are responsible for the enhanced reactivities of these first three radicals relative to the last.

The synergistic impact of multiple fluorine substitution on radical reactivity has been discussed elsewhere in some detail and will not be remarked upon again at this time.[3]

Comments on the bond dissociation energy data

A particularly interesting feature of our BDE calculations is the predicted 2.6 kcal/mol *decrease* in C-H BDE's induced by α,α-difluoro substitution (cf., $CH_3CH_2CH_2\text{-}H = 100.3$ versus $CH_3CH_2CF_2\text{-}H = 97.7$ kcal/mol) and the 4.9 kcal/mol *increase* in C-C BDE's (cf., $CH_3CH_2CH_2\text{-}CH_3 = 86.7$ versus $CH_3CH_2CF_2\text{-}CH_3 = 91.6$ kcal/mol). We believe that these differences are too large to be attributed to uncertainties in the calculations and that they must, therefore, reflect the true situation.

Homolytic C-H BDE's of hydrocarbons bearing heteroatom substituents have long been considered to provide good estimates of the stabilities of the corresponding alkyl radicals.[21] For example, Bordwell and Pasto have devoted considerable attention to the prediction of BDE's of mono- and disubstituted methanes, and they have also presented cogent interpretations of the validity and significance of the derived radical stabilization energies (RSE's), which are defined as the change in the total energy for the isodesmic reaction shown in eq iii, and as such are recognized not to be identical in definition to "resonance" energies.[22,23]

$$X_nCH_{3-n}^{\cdot} + CH_4 \longrightarrow X_nCH_{4-n} + CH_3^{\cdot} \qquad \text{(iii)}$$

Using the experimental bond dissociation energies for the fluorinated methanes [BDE's: $CH_3\text{-}H$ (104.8±0.2), $CH_2F\text{-}H$ (101.2±2), $CHF_2\text{-}H$ (103.2±2), $CF_3\text{-}H$ (106.7±1 kcal/mol)][8,11] indicates that, by equation iii, the impact of fluorine substitution on RSE's is positive for the first fluorine but then increasingly negative along the series. Whereas a single fluorine substituent is stabilizing by 3.6 kcal/mol, two stabilize by a mere 1.6 (which can be compared to the 2.6 kcal/mol stabilization calculated for the $CH_3CF_2^{\cdot}$ radical, compared to $CH_3CH_2^{\cdot}$), and three destabilize by 1.9 kcal/mol. This trend has been explained by Epiotis and Bordwell as deriving from the fact that substituents of the —X: type (that is electronegative substituents bearing lone pairs) should destabilize a radical inductively and stabilize the radical to the extent of their ability to delocalize the odd electron.[24,22] Because the energy of its lone pairs is not conducive to their interaction with the SOMO and with such delocalization further diminishing with increasing pyramidalization, such interaction actually becomes destabilizing for $CF_3^{\cdot}$, which leads to the considerable negative RSE exhibited by $CF_3^{\cdot}$ and hence to the very high CF_3-H BDE. Indeed, because of the strong impact of fluorine substitution on the ground state energies of polyfluoromethanes, one must question the use of RSE values derived from eq iii for evaluating the degree of "radical stabilization" in the fluoromethyl radical series.

There remains the question as to why the C-C BDE's do not also reflect the apparent 1,1-difluoroalkyl radical stabilization which influences the C-H BDE's. The answer to this question lies in the fact that there is a considerable difference in the enthalpies of formation of 1,1-difluoro- and 2,2-difluoroalkanes, which is reflected by the computed isodesmic equation (iv).

$$CH_3CF_2CH_3 + CH_3CH_3 \longrightarrow CH_3CF_2H + CH_3CH_2CH_3 \qquad \text{(iv)}$$
$$\Delta H^\circ = +7.8 \text{ kcal/mol}$$

The large ΔH° value for equation (iv) is best understood in terms of *electrostatics*.[25,26] According to Wiberg, the highly polar C-F bond induces a significant positive charge on the carbon atom, $C^{\delta+}$–$F^{\delta-}$.[26] Moreover, as he has demonstrated in the methane series, the positive charge on carbon increases almost linearly with increasing fluorine substitution, with the negative charge on each of the fluorine substituents remaining constant throughout the series. Wiberg's conclusion was that a consideration of electrostatics (Coulombic attractions) can account for the increase in molecular stabilization as one increases fluorine substitution on methane.

Likewise, we conclude that electrostatics provides a satisfying rationale for the C-C and the C-H BDE data in Tables 2 and 3. Some twenty years ago Rodgers and coworkers postulated that CF_3CH_3 "should have an attractive dipole-dipole interaction" which would strengthen its C-C bond relative to those in ethane or hexafluoroethane.[10,12,13] Such bond strengthening is reflected by isodesmic equations (v) and (vi), the former deriving from experimental heats of formation[27] and the latter from our calculated data.

$$CF_3CF_3 + CH_3CH_3 \rightleftharpoons 2\ CH_3CF_3 \qquad \text{(v)}$$
$$\Delta H^\circ = -16.9 \text{ kcal/mol}$$

$$CH_3CH_2CH_2CH_3 + CH_3CF_2CF_2CH_3 \rightleftharpoons 2\ CH_3CF_2CH_2CH_3 \qquad \text{(vi)}$$
$$\Delta H^\circ = -5.0 \text{ kcal/mol}$$

Figure 1 depicts the atomic charges on CH_2F_2, CH_3CHF_2, and $CH_3CF_2CH_3$ from Table 4. An examination of these charges allows one to conclude that there are strong electrostatic attractions between the carbon atoms in CH_3CHF_2 and in $CH_3CF_2CH_3$, which will, of course, contribute to making the C-C bonds in these two compounds stronger than those in their non-polar counterparts, CH_3CH_3, CF_3CF_3 and CH_3CF_2-CF_2CH_3. In contrast, there would appear to be mild electrostatic repulsion between the α-C and α-H atoms of CH_2F_2 and CH_3CF_2H which will certainly contribute to C-H bond weakening in these compounds. Lastly, and in stark contrast to the situation at the α-carbon, there is a strong electrostatic attraction between the β-C and β-H atoms of CH_3CHF_2 and $CH_3CF_2CH_3$ which is certainly consistent with the observed and calculated increase in the strength of such β C-H bonds.

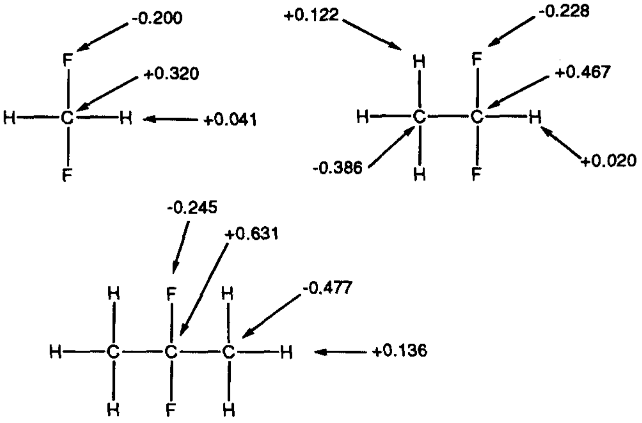


Figure 1. Atomic Charges (MKS-ESP, based on B3LYP/6-31G(d) density)

Thus, simple electrostatics would appear to explain most of the observed effects of fluorine substitution on C-C and C-H BDE's which are reflected in Tables 2 and 3, especially if one also keeps in mind the slight stabilization of $RCF_2^{\cdot}$ radicals and the uniqueness of the CF_3H molecule. Thus we are left with what we believe is a very nice and self-consistent picture of the thermochemistry of bonding and radical stabilization in fluorohydrocarbon systems.

CONCLUSION

In conclusion, the trend of reactivities of partially-fluorinated *n*-alkyl radicals towards hydrogen atom abstraction from *n*-Bu_3SnH is qualitatively similar to that for their addition to alkenes. It has been concluded that the enhanced reactivities of α,α-difluoroalkyl radicals derive largely from their pyramidal nature, whereas the modest increase in β,β-difluoroalkyl radical reactivity is due mostly to thermodynamic factors. Multifluorinated radicals, such as α,α,β,β-tetrafluoro- and perfluoro-*n*-alkyl radicals have exceptional reactivities which derive principally from their enhanced electrophilicity. A computational study of the impact of fluorine substituents on C-H and C-C bond dissociation energies provides new understanding of how fluorine substituents affect bonding in hydrofluorocarbons.

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. All reagents, unless otherwise specified, were purchased from Aldrich, Fisher, PCR, or Acros, and used as received. Styrene (Fisher) was freed from inhibitor by passage through a column of neutral alumina. Dichloromethane was distilled from calcium hydride and used immediately. Diethyl ether was distilled from sodium benzophenone ketyl and used immediately. Benzene was distilled from lithium aluminum hydride and stored over 4 Å molecular sieves. Chloroform, dimethylsulfoxide, and tetraglyme were commercial anhydrous grade. 2-[perfluorohexyl]-1-iodoethane was received as a gift from Prof. N. O. Brace. Preparative gas chromatography was carried out on a 20 ft x 0.25 in. copper column packed with 20% SE-30 on Chromosorb P.

Time Resolved Laser Flash Photolysis. The apparatus and procedures have been described in detail elsewhere.[5] The rate constants for the reactions which resulted in the formation of the benzylic radicals (Scheme 4) were determined from the experimental growth curves of the absorption at ca. 320 nm measured over a range of substrate concentrations, according to eq ii.

Computational Methods. Geometries of various fluorinated ethanes, propanes, and butanes along with their respective radicals generated from terminal C-H or C-CH_3 bond cleavage were optimized at the hybrid density functional level, utilizing Becke's three-parameter method with the correlation functional of Lee, Yang, and Parr[28] and the 6-31G(d) basis. All calculations were performed using the *Gaussian94* program system,[29] utilizing scf=tight convergence criteria and the (75,302)p pruned integration grid. All minima were characterized by vibrational frequency analysis, the resulting zero-point energy correction scaled by 0.9806 as suggested by Scott and Bauschlicher,[30] and a thermal correction of $4RT$ (for C-C BDEs) or $2.5RT$ (for C-H BDEs) applied as recommended by Radom[31] and implemented by Boyd in RHF and MP2 studies of the structure and BDEs of fluorinated ethanes.[7] Where applicable, reported BDEs correspond to those resulting from the lowest electronic energy conformer of the closed-shell species and / or radical. Bond dissociation energies obtained in this fashion were found to be, in the cases where such values are known, within ca. 1-2 kcal / mol of those determined experimentally, and in equal or better agreement with experiment than the MP2/6-311G(d,p)//HF/6-31G(d) and MP2/6-311G(d,p)//MP2/6-31G(d) values obtained by Boyd.[7]

Table 4. Fluorinated Alkanes - Total and (Unscaled) Zero-Point Energies.

Species	**E(B3LYP/6-31G(d)), a.u.**	**ZPE, a.u.**
CH_3CH_3	-79.8304 167	0.075231
CH_3CF_3	-377.5549 235	0.052872
CH_3CF_2H	-278.3015 940	0.061076
CF_3CF_2H	-576.0077 790	0.037905
$CH_3CH_2CH_3$	-119.1442 464	0.104110
$CH_3CF_2CH_3$	-317.6263 447	0.088479
$CF_3CH_2CH_3$	-416.8699 039	0.081649
$CF_3CF_2CH_3$	-615.3356 199	0.065266
$CH_3CH_2CF_2H$ [a]	-317.6163 135	0.089851
$CH_3CH_2CF_2H$ [b]	-317.6162 650	0.090006
$CH_3CF_2CF_2H$ [b]	-516.0884 655	0.073687
$CH_3CF_2CF_2H$ [a]	-516.0853 571	0.073705
$CH_3CH_2CH_2CH_3$ [c]	-158.4580 400	0.132860
$CH_3CH_2CH_2CH_3$ [d]	-158.4567 065	0.132957
$CH_3CH_2CF_2CH_3$ [c]	-356.9408 361	0.117249
$CH_3CH_2CF_2CH_3$ [d]	-356.9401 189	0.117349
$CH_3CF_2CF_2CH_3$ [c]	-555.4151 664	0.101158
$CH_3CF_2CF_2CH_3$ [d]	-555.4110 960	0.101141
$CF_3CH_2CH_2CH_3$ [c]	-456.1836 478	0.110224
$CF_3CH_2CH_2CH_3$ [d]	-456.1826 866	0.110445

a. Methyl and hydrogen gauche; [b]. Methyl and hydrogen anti; [c]. Methyl (or methyl and trifluoromethyl) groups anti; [d]. Methyl (or methyl and trifluoromethyl) groups gauche.

Table 5. Fluorinated Radicals - Total and (Unscaled) Zero-Point Energies.

Species	**E(B3LYP/6-31G(d)), a.u.**	**ZPE, a.u.**
$H\cdot$	-0.5002 728	0
$CH_3\cdot$	-39.8382 909	0.029849
$CF_3\cdot$	-337.5509 879	0.012153
$CH_3CH_2\cdot$	-79.1578 663	0.059647
$CH_3CF_2\cdot$	-277.6352 216	0.047481
$CF_3CH_2\cdot$	-376.8760 847	0.037830
$CF_3CF_2\cdot$	-575.3382 007	0.024522
$CH_3CH_2CH_2\cdot$ [a]	-118.4713 699	0.088731
$CH_3CH_2CH_2\cdot$ [b]	-118.4711 179	0.088945
$CH_3CH_2CF_2\cdot$ [b]	-316.9496 940	0.076574
$CH_3CH_2CF_2\cdot$ [a]	-316.9496 712	0.076368
$CH_3CF_2CH_2\cdot$ [c]	-316.9493 447	0.073435
$CH_3CF_2CH_2\cdot$ [b]	-316.9489 182	0.073225
$CH_3CF_2CF_2\cdot$ [b]	-515.4178 170	0.060271
$CH_3CF_2CF_2\cdot$ [c]	-515.4173 201	0.060276
$CF_3CH_2CH_2\cdot$ [a]	-416.1952 103	0.066154
$CF_3CH_2CH_2\cdot$ [b]	-416.1951 213 [d]	0.066242

[a] Radical p orbital aligned (hyperconjugated) with β C-H bond; [b]. β C-C bond hyperconjugation; [c]. β C-F bond hyperconjugation; [d] Ref. 32

Syntheses of Partially-Fluorinated Alkyl Halides, Reduction Products, and Styrene Adducts.

1,3-Dibromo-1,1-difluorohexane. Based on a modification by Elsheimer[33] of a procedure by Burton,[34] a Carius tube of approximately 200 mL capacity equipped with a small magnetic stir bar was charged with 0.14 g (1.42×10^{-3} mol) cuprous chloride, 4.36 g (7.12×10^{-2} mol) ethanolamine, 12 mL *tert*-butanol, 10.0 g (1.42×10^{-1} mol) 1-pentene, and 59.84 g (2.85×10^{-1} mol) dibromodifluoromethane. The tube was flushed with nitrogen and flame-sealed; upon swirling, a deep blue coloration was observed. The tube was immersed halfway into a silicon oil bath preheated at 85° C and allowed to stir for 48 hours, during which time the coloration turned from deep blue to olive green to brown. *(Caution: this procedure should be performed behind a safety shield.)* The tube was cooled in an ice bath, opened, and the contents transferred to a 250-mL Erlenmeyer flask (at this point, unreacted dibromodifluoromethane may be recovered by distillation) and the tube rinsed with three 50 mL portions of hexanes. All organic material (which consisted of a cloudy yellow-green supernatant and a brown resin) was filtered through 50 mL of silica gel, which was rinsed with two additional 50 mL portions of hexanes. The resulting colorless filtrate was concentrated by rotary evaporation and subject to reduced pressure fractional distillation through a 15 cm Vigreux column. A total of 22.79 g (57.3%) of the title compound was obtained as a colorless liquid, bp 80-85° C / 25 mm Hg. ^{1}H NMR: δ 0.96 (3H, t, $^{3}J_{HH}$ = 7.42 Hz), 1.50 (2H, m), 1.86 (2H, m), 3.01 (2H, m), 4.24 (1H, m); ^{13}C NMR: δ 13.2, 20.4, 40.5, 46.6, 52.7 (t, $^{2}J_{CF}$ = 21.8 Hz), 120.6 (t, $^{1}J_{CF}$ = 306.9 Hz); ^{19}F NMR: ϕ -43.2 (m); HRMS for $C_6H_{10}F_2Br_2$: calc. 277.9117, calc. (M-Br) 198.9934, found 198.9983; CHN for $C_6H_{10}F_2Br_2$: calc. 25.74% C, 3.60% H, found 25.53% C, 3.43% H.

1-Bromo-1,1-difluorohexane and 1,1-difluorohexane. A 250 mL three-necked round-bottomed flask equipped with an ice-water condenser, argon inlet, and magnetic stir bar was charged with 20.0 g (7.14×10^{-2} mol) 1,3-dibromo-1,1-difluorohexane dissolved in 100 mL anhydrous dimethylsulfoxide. A total of 10.8 g (2.85×10^{-1} mol) of sodium borohydride was then added in small portions with vigorous stirring over the course of 1 hour, during which time the flask became warm and a semisolid gel was observed to form. After the addition was complete, the bath temperature was raised to 70° C over the course of 1 hour and heating continued for an additional 6 hours (^{19}F NMR analysis of a small aliquot of the reaction mixture at this time showed complete consumption of starting material.) The flask was cooled to room temperature, the contents transferred to a 1 L Erlenmeyer flask, and the reaction quenched with chips of ice. The resulting mixture was *carefully* acidified with concentrated aqueous HCl, 100 mL ether was added, and the aqueous / DMSO layer extracted with three 50 mL portions of ether. The combined ether layers were washed with three 25 mL portions of water, dried over $MgSO_4$, and subject to ambient pressure fractional distillation through a 15 cm Vigreux column. After concentration in this way, 8.91 g (62.1%) of 1-bromo-1,1-difluorohexane (contaminated with a small amount of 1,1-difluorohexane) was obtained as a colorless liquid, bp 125-128° C. Preparative GC separation afforded analytically pure samples of each. For 1-bromo-1,1-difluorohexane: ^{1}H NMR: δ 0.92 (3H, t, $^{3}J_{HH}$ = 7.5 Hz), 1.35 (4H, m), 1.62 (2H, m), 2.33 (2H, m); ^{13}C NMR: δ 13.8, 22.3, 23.6, 30.6, 44.3 (t, $^{2}J_{CF}$ = 21.1 Hz), 123.3 (t, $^{1}J_{CF}$ = 303.5 Hz); ^{19}F NMR: ϕ -43.9 (t, $^{3}J_{FH}$ = 14.7 Hz); HRMS for $C_6H_{11}F_2Br$: calc. 200.0012, calc. (M-Br) 121.0829, found 121.0832; CHN for $C_6H_{11}F_2Br$: calc. 35.84% C, 5.51% H, found 35.47% C, 5.54% H. For 1,1-difluorohexane: ^{1}H NMR: δ 0.91 (3H, t, $^{3}J_{HH}$ = 6.9 Hz), 1.34 (4H, m), 1.45 (2H, m), 1.80 (2H, m), 5.79 (1H, tt, $^{3}J_{HH}$ = 4.5 Hz, $^{2}J_{HF}$ = 57 Hz); ^{13}C NMR: δ 13.8, 21.8 (t, $^{3}J_{CF}$ = 5.5 Hz), 22.4, 31.2, 34.1 (t, $^{2}J_{CF}$ = 20.6 Hz), 117.5 (t, $^{1}J_{CF}$ = 237.4 Hz); ^{19}F NMR: ϕ -116.3 (dt, $^{3}J_{FH}$ = 17.1 Hz, $^{2}J_{FH}$ = 56.2 Hz); HRMS for $C_6H_{12}F_2$: calc. 122.0907, calc. (M-H) 121.0829, found 121.0825.

1-Phenyloctan-3-ol. Into a flame-dried 300 mL three-necked round-bottomed flask equipped with a 125 mL pressure-equalizing addition funnel, condenser with argon inlet, and magnetic stir bar was dispensed 3.94 g (1.62 x 10^{-1} mol) Mg turnings and a small crystal of iodine. 10.0 g (5.40 x 10^{-2} mol) of (2-bromoethyl)benzene was dissolved in 100 mL of anhydrous ether and added to the funnel. After addition of a small amount of solution and initiation of the reaction, addition was continued at a rate that maintained gentle reflux, after which time the mixure was refluxed for an additional 2 hours. The flask was then cooled to room temperature and 5.41 g (5.40 x 10^{-2} mol) of hexanal was dissolved in 50 mL anhydrous ether, added to the addition funnel and dispensed dropwise at a rate that maintained gentle reflux. The mixture was refluxed for an additional 2 hours, cooled to room temperature, and quenched with a mixture of 100 g of ice and 50 mL concentrated aqueous HCl. The layers were separated, the aqueous layer extracted with three 50 mL portions of ether, and the combined organic extracts washed twice with 20 mL 5% aqueous $NaHCO_3$ and once with 20 mL of water. The organic layer was dried over $MgSO_4$, the solvent rotary evaporated, and the resulting liquid subjected to reduced pressure fractional distillation through a 15 cm Vigreux column. 8.75 g (78.7%) of the desired alcohol was obtained as a colorles liquid, bp 148-151° C / 0.1 mm Hg. ^{1}H NMR: δ 0.94 (3H, t, $^3J_{HH}$ = 5.7 Hz), 1.34 (4H, m), 1.51 (4H, m), 1.81 (2H, m), 2.76 (2H, m), 3.67 (1H, m), 7.28 (5H, m); ^{13}C NMR: δ 14.0, 22.6, 25.2, 31.8, 32.0, 37.5, 39.0, 71.4, 125.7, 128.3, 128.4, 142.2; HRMS for $C_{14}H_{22}O$: calc. 206.1671, found 206.1672.

1-Phenyloctan-3-one. Into a 100 mL round-bottomed flask was placed 3.8 g (1.84 x 10^{-2} mol) of 1-phenyloctan-3-ol dissolved in 10 mL ether. 8.5 mL of previously prepared Jones' reagent (5.0 g $Na_2Cr_2O_7$ and 3.65 mL concentrated H_2SO_4 diluted with water to a total volume of 25 mL) was added dropwise to the alcohol solution with stirring, and allowed to react for 4 hours at room temperature. The dark green reaction mixture was diluted with 20 mL ether and 20 mL water. The aqueous layer was extracted with three 20 mL portions of ether, and the combined organic extracts washed twice with 20 mL saturated $NaHCO_3$, once with 20 mL brine, and dried over $MgSO_4$. Rotary evaporation of the solvent followed by reduced pressure fractional distillation through a 10 cm Vigreux column afforded 3.34 g (89.0%) of the desired ketone, bp 108-111° C / 0.35 mm Hg. ^{1}H NMR: δ 0.87 (3H, t, $^3J_{HH}$ = 6.9 Hz), 1.26 (4H, m), 1.55 (2H, overlapping tt, $^3J_{HH}$ = 7.5 Hz), 2.37 (2H, t, $^3J_{HH}$ = 7.2 Hz), 2.72 (2H, m), 2.89 (2H, m), 7.23 (5H, m); ^{13}C NMR: δ 13.9, 22.4, 23.5, 29.8, 31.4, 43.0, 44.2, 126.0, 128.3, 128.4, 141.2, 210.3; HRMS for $C_{14}H_{20}O$: calc. 204.1514, found 204.1532; CHN for $C_{14}H_{20}O$: calc. 82.30% C, 9.87% H, found 82.53% C, 10.14% H.

3,3-Difluoro-1-phenyloctane. Into a 100 mL three-necked round-bottomed flask equipped with stir bar, rubber septum, and condenser with argon inlet was placed 2.0 g (9.80 x 10^{-3} mol) of 1-phenyloctan-3-one dissolved in 15 mL anhydrous CH_2Cl_2. Into the reaction mixture was slowly injected 1.74 g (1.08 x 10^{-2} mol) diethylaminosulfurtrifluoride (DAST) with stirring, during which time the flask became slightly warm. The mixture was heated at reflux for 72 hours, over which time a dark amber coloration was observed. After cooling, the reaction mixture was carefully decanted onto 50 mL of ice water and diluted with 10 mL CH_2Cl_2. The organic layer was separated and the aqueous layer extracted with three 20 mL portions of CH_2Cl_2. The combined organic extracts were washed once with 10 mL of 10% aqueous $NaHCO_3$ and once with 10 mL water, dried over $MgSO_4$, and the solvent rotary evaporated. Fractional reduced pressure distillation of the resulting liquid afforded 1.66 g (68.0%) of 3,3-difluoro-1-phenyloctane, bp 100-105° C / 0.2 mm Hg. ^{1}H NMR: δ 0.92 (3H, t, $^3J_{HH}$ = 6.3 Hz), 1.33 (4H, m), 1.48 (2H, m), 1.87 (2H, m), 2.13 (2H, m), 2.82 (2H, m), 7.27 (5H, m); ^{13}C NMR: δ 13.9, 22.0, 22.4, 28.5, 31.5, 36.5 (t, $^2J_{CF}$ = 25.1 Hz), 38.2 (t, $^2J_{CF}$ = 25.5 Hz), 124.8 (t, $^1J_{CF}$ = 239.4 Hz), 126.1, 128.3, 128.5, 140.8); ^{19}F NMR: ϕ -99.1 (overlapping tt, $^3J_{FH}$ = 17.1 Hz); HRMS for $C_{14}H_{20}F_2$:

calc. 226.1533, found 226.1529; CHN for $C_{14}H_{20}F_2$: calc. 74.30% C, 8.91% H, found 74.14% C, 9.15% H.

1-Bromohexan-2-one. Based on a procedure by Zav'yalov,[35] into a 250 mL three-necked round-bottomed flask equipped with an argon inlet, magnetic stir bar, and 100 mL pressure-equalizing addition funnel was placed 10.0 g (9.98×10^{-2} mol) of 2-hexanone, 40 mL glacial acetic acid, and 9.75 g (1.62×10^{-1} mol) urea. The flask was cooled to 0° C and 17.15 g (1.07×10^{-1} mol) of bromine was introduced dropwise into the reaction mixture over the course of 1 hour. After the addition was complete, the cooling bath was removed and the reaction mixture allowed to warm to room temperature and stirred overnight. The contents were then transferred to a separatory funnel, diluted with 200 mL water, and extracted with four 50 mL portions of CH_2Cl_2. The combined organic extracts were washed with three 20 mL portions of 10% aqueous $NaHCO_3$, dried over $MgSO_4$, and the solvent rotary evaporated. Fractional reduced pressure distillation through a 15 cm Vigreux column yielded 12.91 g (72.2%) of the desired 1-bromoketone, contaminated with ca. 6% (by ^{1}H NMR) of the 3-bromo isomer, bp 85-88° C / 15 mm Hg. Column chromatography (silica gel, 20% ethyl acetate in hexanes) of a small sample yielded pure 1-bromohexan-2-one, which was used in characterization. ^{1}H NMR: δ 0.91 (3H, t, $^3J_{HH} = 7.5$ Hz), 1.33 (2H, overlapping tt, $^3J_{HH} = 7.5$ Hz), 1.60 (2H, overlapping tt, $^3J_{HH} = 7.5$ Hz), 2.64 (2H, t, $^3J_{HH} = 7.2$ Hz), 3.88 (2H, s); ^{13}C NMR: δ 13.7, 22.1, 25.9, 34.3, 39.5, 202.2; HRMS for $C_6H_{11}BrO$: calc. 177.9993, found 177.9934; CHN for $C_6H_{11}BrO$: calc. 40.25% C, 6.19% H, found 40.10% C, 6.19% H. *(Caution: α-bromoketones are powerful lachrymators.)*

1-Bromo-2,2-difluorohexane. A 100 mL three-necked round-bottomed flask equipped with magnetic stir bar, condenser with argon inlet, and rubber septum was charged with 5.0 g (2.79×10^{-2} mol) 1-bromohexan-2-one dissolved in 20 mL anhydrous $CHCl_3$. 9.15 g (5.68×10^{-2} mol) DAST was slowly injected into the reaction mixture, which was then heated at 50° C for 48 hours. The flask was cooled and the contents carefully dispensed into 50 mL of ice water. The layers were separated, the aqueous layer extracted with three 5 mL portions of CH_2Cl_2, and the combined organic extracts washed twice with 10 mL portions of 10% aqueous $NaHCO_3$ and once with 10 mL of water. Drying over $MgSO_4$, evaporation of the halogenated solvents by ambient-pressure distillation through a 10 cm Vigreux column, and fractional, ambient pressure distillation afforded 3.35 g (59.7%) of the title compound as a colorless liquid, bp 120-122° C. ^{1}H NMR: δ 0.94 (3H, t, $^3J_{HH} = 7.2$ Hz), 1.42 (4H, m), 2.02 (2H, m), 3.51 (2H, t, $^3J_{HF} = 13.2$ Hz); ^{13}C NMR: 13.7, 22.3, 24.1, 31.4 (t, $^2J_{CF} = 34.1$ Hz), 34.2 (t, $^2J_{CF} = 24.0$ Hz), 121.5 (t, $^1J_{CF} = 240.9$ Hz); ^{19}F NMR: ϕ -99.2 (m); HRMS for $C_6H_{11}F_2Br$: calc. 200.0012, calc. (M-H) 198.9934, found 198.9974; CHN for $C_6H_{11}F_2Br$: calc. 35.84% C, 5.51% H, found 36.00% C, 5.48% H. This material was further purified by preparative GC for use in the kinetic study; however, a sluggish chain reaction with this bromide precursor led us to the preparation of the iodo precursor below.

1-Iodo-2,2-difluorohexane. 2.0 g (9.95×10^{-3} mol) of 1-bromo-2,2-difluorohexane was placed into a thick-walled Carius tube of approximately 150 mL capacity, along with a small magnetic stir bar. 100 mL of a hot saturated solution of sodium iodide in acetone was added to the tube, which was then cooled in a dry ice-isopropanol slush and flame-sealed. After warming to room temperature, the tube was immersed halfway in an oil bath atop a magnetic stirrer. The mixture was stirred at 85-90° C for 96 hours (a safety shield is recommended) at which time the tube was cooled, opened, and the contents transferred to a 250 mL round-bottomed flask. Most of the solvent was removed by rotary evaporation, and the remaining residue taken up in a mixture of 50 mL of water and 50 mL of ether. The layers were separated, the aqueous layer extracted with three 50 mL portions of ether, and the combined organic extracts washed with 20 mL of water. Drying over $MgSO_4$, rotary evaporation of the solvent, and fractional reduced-pressure distillation afforded 2.16 g (87.5%) of very pure 1-iodo-2,2-difluorohexane: bp 101-102° C / 68 mm Hg. ^{1}H NMR: δ 0.93 (3H, t, $^3J_{HH}$ = 7.2 Hz); 1.41 (4H, m), 2.06 (2H, m), 3.40 (2H, t, $^3J_{HF}$ = 14.4 Hz); ^{13}C NMR: δ 3.95 (t, $^2J_{CF}$ = 31.5 Hz), 13.7, 22.3, 24.4, 35.0 (t, $^2J_{CF}$ = 24.5 Hz), 121.1 (t, $^1J_{CF}$ = 240.8 Hz); ^{19}F NMR: ϕ -94.9 (overlapping tt, $^3J_{FH}$ = 17.1 Hz); HRMS for $C_6H_{11}F_2I$: calc. 247.9833, found 247.9862; CHN for $C_6H_{11}F_2I$: calc. 29.05% C, 4.47% H, found 28.82% C, 4.48% H.

2,2-Difluorohexane. 1.0 g (4.97 x 10^{-3} mol) of 1-bromo-2,2-difluorohexane was dissolved in 5 mL benzene in a 25 mL round-bottomed flask equipped with septum-capped sidearm inlet and magnetic stir bar, and attached to a small distillation apparatus equipped with with ice water condenser and fractionating column. The bath temperature was raised to 60° C and 1.60 g (5.50 x 10^{-3} mol) nBu_3SnH and 0.01 g (6.09 x 10^{-5} mol) 2,2'-Azobisisobutyronitrile (AIBN) dissolved in 0.5 mL benzene was added slowly via syringe through the rubber septum. When the addition was complete, the mixture was stirred for an additional 30 minutes and the bath temperature quickly raised to 150° C. All volatile material was flash distilled and subjected to preparative GC separation which afforded analytically pure 2,2-difluorohexane as a colorless liquid: ^{1}H NMR: δ 0.92 (3H, t, $^3J_{HH}$ = 7.2 Hz), 1.42 (4H, m), 1.58 (3H, t, $^3J_{HF}$ = 18.3 Hz), 1.83 (2H, m); ^{13}C NMR: δ 13.8, 22.5, 23.2 (t, $^2J_{CF}$ = 28.1 Hz), 24.9 (t, $^3J_{CF}$ = 4.5 Hz), 37.7 (t, $^2J_{CF}$ = 25.1 Hz), 124.5 (t, $^1J_{CF}$ = 236.4 Hz); ^{19}F NMR: ϕ -90.9 (m); HRMS for $C_6H_{12}F_2$: calc. 122.0907, calc. (M-HF) 102.0845, found 102.0822.

1-Phenyloctan-4-ol. In a manner similar to that of the preparation of 1-phenyloctan-3-ol, 10.0 g (5.02 x 10^{-2} mol) of 1-bromo-3-phenylpropane dissolved in 100 mL anhydrous ether was added to 3.67 g (1.51 x 10^{-1} mol) Mg turnings to which a crystal of iodine had been added. Subsequent addition of 4.54 g (5.27 x 10^{-2} mol) of valeraldehyde dissolved in 50 mL anhydrous ether followed by workup in the usual way afforded 7.36 g (71.1%) the title compound, bp 102-103° C / 0.05 mm Hg. ^{1}H NMR: δ 0.91 (3H, t, $^3J_{HH}$ = 6.6 Hz), 1.52 (10H, overlapping m), 2.65 (2H, t, $^3J_{HH}$ = 7.5 Hz), 3.62 (1H, m), 7.24 (5H, m); ^{13}C NMR: 14.0, 22.7, 27.4, 27.8, 35.9, 37.0, 37.1, 71.7, 125.7, 128.2, 128.3, 142.4; HRMS for $C_{14}H_{22}O$: calc. 206.1671, found 206.1671; CHN for $C_{14}H_{22}O$: calc. 81.50% C, 10.75% H, found 81.72% C, 10.92% H.

1-Phenyloctan-4-one. In a manner similar to that of the preparation of 1-phenyloctan-3-one, 15 mL of Jones' reagent was added to 5.0 g (2.42 x 10^{-2} mol) 1-phenyloctan-4-ol in 25 mL ether. Workup in the usual way followed by distillation at reduced pressure yielded 4.14 g (83.7%) the title compound, bp 123-125° C / 0.4 mm Hg. ^{1}H NMR: δ 0.96 (3H, t, $^3J_{HH}$ = 7.2 Hz), 1.36 (2H, m), 1.60 (2H, m), 1.97 (2H, overlapping tt, $^3J_{HH}$ = 7.5 Hz), 2.46 (4H, m), 2.69 (2H, t, $^3J_{HH}$ = 7.2 Hz), 7.30 (5H, m); ^{13}C NMR: 13.8, 22.3, 25.2, 25.8, 35.0, 41.8, 42.5, 125.8, 128.3, 128.4, 141.6, 211.0; HRMS for $C_{14}H_{20}O$: calc. 204.1514, found 204.1576; CHN $C_{14}H_{20}O$: calc. 82.30% C, 9.87% H, found 82.40% C, 9.83% H.

4,4-Difluoro-1-phenyloctane. In a manner similar to the preparation of 3,3-difluoro-1-phenyloctane, 2.5 g (1.22 x 10^{-2} mol) 1-phenyloctan-4-one and 3.93 g (2.44 x 10^{-2} mol) DAST in 25 mL CH_2Cl_2 were refluxed for 48 hours. Workup in the usual way afforded 1.83 g (66.3%) 4,4-difluoro-1-phenyloctane: bp 85-88° C / 0.1 mm Hg. ^{1}H NMR: δ 0.89 (3H, t, $^3J_{HH}$ = 6.9 Hz), 1.34 (4H, m), 1.80 (6H, m), 2.63 (2H, t, $^3J_{HH}$ = 6.9 Hz), 7.22 (5H, m); ^{13}C NMR: δ 13.8, 22.5, 24.0 (t, $^3J_{CF}$ = 4.5 Hz), 24.38 (t, $^3J_{CF}$ = 4.7 Hz), 35.4, 35.7 (t, $^2J_{CF}$ = 26.0 Hz), 36.1 (t, $^2J_{CF}$ = 25.1 Hz), 125.2 (t, $^1J_{CF}$ = 238.9 Hz), 125.9, 128.4 (2C, overlapping), 141.5; ^{19}F NMR: ϕ -98.3 (overlapping tt, $^3J_{FH}$ = 17.1 Hz); HRMS for $C_{14}H_{20}F_2$: calc. 226.1533, found 226.1533; CHN for $C_{14}H_{20}F_2$: calc. 74.30% C, 8.91% H, found 74.40%C, 8.85% H.

1-Bromo-1,1,2,2-tetrafluorohexane. Into a 250-mL three-necked round-bottomed flask equipped with a magnetic stir bar, rubber septum, and condenser equipped with an argon inlet was added 36 mL tetraglyme and 30.0 g (1.28×10^{-1} mol) of 6-bromo-5,5,6,6-tetrafluorohex-1-ene (obtained as a gift from Halocarbon, Inc.) 24 mL of a 2.0 M solution of borane · dimethyl sulfide in diethyl ether (4.80×10^{-2} mol) was slowly injected into the flask through the septum. Some bubbling was evident and the flask became slightly warm. This mixture was stirred for two hours at room temperature then heated at reflux with stirring overnight. The flask was then cooled to room temperature and 64 mL (59.3 g, 5.11×10^{-1} mol) of hexanoic acid was slowly injected into the reaction mixture with stirring. Vigorous bubbling was evident and the flask became warm. Stirring was continued for 2 hours at room temperature then at reflux overnight. The mixture was distilled through a 15 cm Vigreux column at ambient pressure until the head temperature reached 140° C, at which time distillation ceased. The distillate was diluted with 50 mL of ether, washed with two 10 mL portions of saturated aqueous sodium bicarbonate and two 10 mL portions of water, dried, and the resulting solution distilled at ambient pressure. After removal of ether and residual dimethyl sulfide in this way, 24.16 g (79.6%) of 1-bromo-1,1,2,2-tetrafluorohexane was obtained as a colorless liquid boiling at 122-124° C. ^{1}H NMR: δ 0.95 (3H, t, $^3J_{HH} = 7.2$ Hz), 1.41 (2H, m), 1.59 (2H, m), 2.07 (2H, m); ^{13}C NMR: δ 13.7, 22.3, 22.6, 30.1 (t, $^2J_{CF} = 22.5$ Hz), 117.5 (tt, $^2J_{CF} = 31.1$ Hz, $^1J_{CF} = 251.8$ Hz,), 118.0 (tt, $^2J_{CF} = 39.6$ Hz, $^1J_{CF} = 309.5$ Hz,); ^{19}F NMR: ϕ -65.9 (2F, s), -112.6 (2F, t, $^3J_{FH} = 19.5$ Hz); HRMS for $C_6H_9F_4Br$: calc. 235.9823, calc. (M+H) 236.9902, found 236.9738; CHN for $C_6H_9F_4Br$: calc. 30.40% C, 3.83% H, found 30.72% C, 3.46% H.

1,1,2,2-Tetrafluorohexane. 2.0 g (8.44×10^{-3} mol) 1-bromo-1,1,2,2-tetrafluorohexane was dissolved in 5 mL of benzene in a 25 mL round-bottomed flask equipped with septum-capped sidearm inlet and stir bar, and attached to a small distillation apparatus equipped with ice water condenser and fractionating column. The bath temperature was raised to 60° C and 2.95 g (1.01×10^{-2} mol) nBu_3SnH and 0.01 g (6.09×10^{-5} mol) AIBN dissolved in 0.5 mL benzene was added slowly via syringe through the rubber septum. When the addition was complete, the mixture was stirred for an additional 30 minutes and the bath temperature quickly raised to 150° C. All volatile material was flash distilled and subjected to preparative GC separation which afforded pure 1,1,2,2-tetrafluorohexane as a colorless liquid. ^{1}H NMR: δ 0.95 (3H, t, $^3J_{HH} = 7.5$ Hz), 1.40 (2H, m), 1.55 (2H, m), 1.95 (2H, m), 5.70 (1H, tt, $^3J_{HF} = 3.0$ Hz, $^2J_{HF} = 54.0$ Hz); ^{13}C NMR: 13.6, 22.4 (2C, overlapping), 29.6 (t, $^2J_{CF} = 22.5$ Hz), 110.4 (tt, $^2J_{CF} = 41.1$ Hz, $^1J_{CF} = 248.4$ Hz), 118.1 (tt, $^2J_{CF} = 28.5$ Hz, $^1J_{CF} = 243.8$ Hz); ^{19}F NMR: ϕ -116.8 (2F, t, $^3J_{FH} = 19.5$ Hz), -136.1 (2F, d, $^2J_{FH} = 53.7$ Hz); HRMS for $C_6H_{10}F_4$: calc. 158.0719, calc. (M-H) 157.0640, found 157.0648.

3,3,4,4-Tetrafluoro-1-phenyloctane. 2.0 g (8.44×10^{-3} mol) 1-bromo-1,1,2,2-tetrafluorohexane and 1.76 g (1.69×10^{-2} mol) styrene dissolved in 25 mL benzene were added to a 100 mL three-necked round-bottomed flask fitted with rubber septum, condenser with argon inlet, and magnetic stirrer. 4.90 g (1.68×10^{-2} mol) nBu_3SnH and 0.05 g (3.04×10^{-4} mol) AIBN were dissolved in 5 mL benzene and taken up in a syringe. A 150 W flood lamp was placed at a distance of approximately 15 cm from the flask, and with irradiation (at this distance, sufficient heat was generated to cause the solvent to reflux as well) the nBu_3SnH solution was delivered to the reaction mixture via syringe pump over a 36 hour period. After rotary evaporation at elevated temperature, column chromatography (silica gel, hexanes) afforded four fractions of 3,3,4,4-tetrafluoro-1-phenyloctane which were free from organotin contaminants. ^{1}H NMR: δ 0.96 (3H, t, $^3J_{HH} = 7.2$ Hz), 1.41 (2H, m), 1.57 (2H, m), 2.02 (2H, m), 2.31 (2H, m), 2.90 (2H, m), 7.28 (5H, m) ^{13}C NMR: 1.0, 13.8, 22.5, 26.9, 29.7 (t, $^2J_{CF} = 22.7$ Hz), 32.1 (t, $^2J_{CF} = 22.8$ Hz), 118.8 (tt, $^2J_{CF} = 37.6$ Hz, $^1J_{CF} = 250.4$ Hz); 119.3 (tt, $^2J_{CF} = 34.1$ Hz, $^1J_{CF} = 245.9$ Hz), 126.3, 128.3, 128.6, 140.3); ^{19}F NMR: ϕ -116.0 (2F, m), -116.4 (2F, m); HRMS for $C_{14}H_{18}F_4$: calc. 262.1345, found 262.1307.

1,1,2,2-Tetrafluoro-1,4-diiodobutane. In accordance with a procedure by Rondestvedt,[36] into a stainless steel pressure reactor of approximately 700 mL capacity was added 100 g (2.83×10^{-1} mol) of 1,2-diiodotetrafluoroethane and 0.5 g (3.67×10^{-3} mol) of *d*-limonene. The reactor was tightly sealed, connected to a vacuum line, immersed in a liquid nitrogen bath, and subjected to three successive freeze-pump-thaw cycles to remove oxygen. 15.86 g (5.65×10^{-1} mol) of ethylene was then transferred into the bomb, which was then sealed and placed into a heating manifold. *(Caution: the following is performed behind a safety shield.)* The thermostat was then set at 210° C, and with constant stirring the reaction mixture was heated for 8 hours. After cooling in an ice bath, venting, and opening, the contents (a dark violet liquid and dark solid) were diluted with 50 mL $CHCl_3$, transferred to a 250 mL Erlenmeyer flask, and chilled in a freezer at -20° C, which caused precipitation of a large amount of dark solid. The mixture was filtered, the solid washed with three 20 mL portions of cold $CHCl_3$, and the combined organic liquids rotary evaporated at room temperature. The remaining liquid was fractionally distilled at reduced pressure through a 15 cm Vigreux column. A total of 43.36 g (40.1%) of the title compound was obtained as a violet liquid, bp 82-85° C / 22 mm Hg. ^{1}H NMR: δ 2.70 (2H, m), 3.24 (2H, m); ^{13}C NMR: δ -10.5, 34.7 (t, $^2J_{CF} = 22.7$ Hz), 96.7 (tt, $^2J_{CF} = 42.8$ Hz, $^1J_{CF} = 315.9$ Hz), 116.5 (tt, $^2J_{CF} = 30.9$ Hz, $^1J_{CF} = 253.1$ Hz); ^{19}F NMR: ϕ -60.8 (2F, t, $^3J_{FF} = 4.9$ Hz), -108.9 (2F, tt, $^3J_{FF} = 4.9$ Hz, $^3J_{FH} = 17.0$ Hz).

3,3,4,4-Tetrafluoro-4-iodobut-1-ene. Into a 250 mL three-necked round-bottomed flask equipped with magnetic stir bar, argon inlet, and pressure-equalizing addition funnel was added 30.69 g (8.03×10^{-2} mol) 1,1,2,2-tetrafluoro-1,4-diiodobutane dissolved in 60 mL anhydrous ether. 26.88 g (1.77×10^{-1} mol) DBU dissolved in 50 mL anydrous ether was added dropwise at room temperature and allowed to stir for an additional 6 hours; at this time, ^{19}F NMR analysis of a small aliquot of the reaction mixture showed complete consumption of starting material. The mixture was poured into 50 mL of 5% aqueous HCl, the layers separated, and the aqueous phase extracted with three 10 mL portions of ether. The combined organic fractions were washed once with 20 mL of saturated $NaHCO_3$ solution, once with 10 mL of water, dried over $MgSO_4$, and the ether carefully removed by gentle, ambient pressure distillation through a 15 cm Vigreux column. Upon removal of most of the solvent in this way, the bath temperature was increased and 13.46 g (66.0%) of the title compound was collected over a range of 90-92° C. ^{1}H NMR: δ 5.83 (1H, m), 5.99 (2H, m); ^{13}C NMR: δ 97.3 (tt, $^2J_{CF} = 44.1$ Hz, $^1J_{CF} = 316.5$ Hz), 113.5 (tt, $^2J_{CF} = 30.1$ Hz, $^1J_{CF} = 249.9$ Hz), 124.2 (t, $^2J_{CF} = 26.1$ Hz), 126.0 (t, $^3J_{CF} = 8.6$ Hz); ^{19}F NMR: ϕ -60.7 (2F, t, $^3J_{FH} = 7.3$ Hz), -108.7 (2F, m).

1,1,2,2-Tetrafluoro-1-iodobutane. Into a 250 mL three-necked round-bottomed flask equipped with reflux condenser, pressure-equalizing addition funnel and magnetic stir bar was added 10.0 g (3.94×10^{-2} mol) of 3,3,4,4-tetrafluoro-4-iodobut-1-ene dissolved in 50 mL of dry methanol, 3.20 g (9.98×10^{-2} mol) anhydrous hydrazine, and 0.1 g (1.01×10^{-3} mol) cuprous chloride. The flask was cooled to 0° C, and 14.2 g of a 30% aqueous solution of hydrogen peroxide was delivered dropwise over a period of 20 minutes, over which time the color of the reaction mixture changed to powder blue then to a dark amber as the H_2O_2 addition neared completion. The cooling bath was then removed, the mixture allowed to stir at room temperature for an additional 2 hours, and the contents poured into a solution of 1 mL of concentrated HCl in 200 mL of water. The mixture was extracted with six 10 mL portions of 1,2-dichlorobenzene, dried over Na_2SO_4, and transferred to a 100 mL flask attached to a 15 cm Vigreux column. A vaccuum adapter attached to small trap (immersed in a dry ice-isopropanol slush) was attached, the pressure lowered to 100 mm Hg, and the flask heated with vigorous stirring until the contents began to boil. At this time, it was observed that approximately 1 mL of material had accumulated in the trap, which was subjected to preparative GC separation. A total of 1.08 g (10.7%) of 1,1,2,2-tetrafluoro-1-iodobutane was collected as a colorless liquid. ^{1}H NMR: δ 1.15 (3H, t, $^3J_{HH} =$

7.5 Hz), 2.11 (2H, m); ^{13}C NMR: 5.05, 23.0 (t, $^{2}J_{CF}$ = 23.6 Hz); 98.5 (tt, $^{2}J_{CF}$ = 43.5 Hz, $^{1}J_{CF}$ = 315.9 Hz); 117.5 (tt, $^{2}J_{CF}$ = 29.6 Hz, $^{1}J_{CF}$ = 250.9 Hz); ^{19}F NMR: ϕ -59.9 (2F, t, $^{3}J_{FF}$ = 4.9 Hz), -110.4 (2F, tt, $^{3}J_{FF}$ = 4.9 Hz, $^{3}J_{FH}$ = 17.1 Hz).

Pentafluoroethane. 2.16 g (8.78 x 10^{-3} mol) of iodopentafluoroethane, was condensed into a Pyrex tube equipped with a Rotaflo stopcock, rubber septum, and immersed in a dry ice-isopropanol slush. 3.07 g (1.05 x 10^{-2} mol) nBu$_3$SnH was injected into the tube and the stopcock closed. The tube was then subjected to photolysis in a Rayonet reactor for 30 minutes at room temperature with periodic shaking. The tube was cooled to -20° C in a dry ice-isopropanol bath, a rubber hose connected to the Rotaflo tube and to a trap immersed in a liquid nitrogen-ether slush, and the stopcock opened. After trap-to-trap transfer in this way, an NMR tube containing ca. 1 mL CDCl$_3$, capped with a rubber septum, and immersed in a liquid-nitrogen-ether slush was connected via cannula. The trap was warmed to -20° C as a sample of pentafluoroethane collected in the tube, which was flame sealed and taken for NMR analysis. ^{1}H NMR: δ 5.88 (tq, $^{3}J_{HF}$ = 2.4 Hz, $^{2}J_{HF}$ = 52.2 Hz); ^{19}F NMR: ϕ -86.1 (3F, s), -138.5 (2F, d, $^{2}J_{FH}$ = 51.3 Hz).

1,1,1,2,2-Pentafluoro-4-phenylbutane. 5.47 g (2.22 x 10^{-2} mol) of iodopentafluoroethane was condensed into a Pyrex Rotaflo tube containing 2.12 g (2.04 x 10^{-2} mol) styrene, 5.92 g (2.03 x 10^{-2} mol) nBu$_3$SnH, 5 mL benzene and a small sir bar. The stopcock was closed and the tube irradiated with a 150 W flood lamp with stirring for 72 hours. Volatiles were removed by rotary evaporation and the residue subject to flash vaccuum distillation at 100 mm Hg (bath temperature 150° C) during which time the distillate temperature reached 69° C. Preparative GC purification of the distillate yielded an analytically pure sample of 1,1,1,2,2-pentafluoro-4-phenylbutane. ^{1}H NMR: δ 2.38 (2H, m), 2.95 (2H, m), 7.31 (5H, m); ^{13}C NMR: δ 26.6, 32.7 (t, $^{2}J_{CF}$ = 21.5 Hz), 115.5 (tq, $^{2}J_{CF}$ = 37.6 Hz, $^{1}J_{CF}$ = 250.4 Hz), 119.3 (qt, $^{2}J_{CF}$ = 36.1 Hz, $^{1}J_{CF}$ = 283.4 Hz), 126.7, 128.2, 128.8, 139.2; ^{19}F NMR: ϕ -85.9 (3F, s), -119.1 (2F, t, $^{3}J_{FH}$ = 19.5 Hz); HRMS for $C_{10}H_9F_5$: calc. 224.0624, found 224.0670; CHN for $C_{10}H_9F_5$: calc. 53.58% C, 4.05% H, found 53.42%C, 3.97% H.

1-[Perfluorohexyl]ethane. Into a 25 mL round-bottomed flask equipped with septum-capped sidearm inlet and magnetic stir bar was placed 4.22 g (8.90 x 10^{-3} mol) 2-[perfluorohexyl]-1-iodoethane. The flask was attached to a distillation apparatus equipped with a small fractionating column and ice water condenser. The bath temperature was raised to 80° C and 3.11 g (1.07 x 10^{-2} mol) nBu$_3$SnH was slowly injected into the flask with stirring. After 30 minutes at this temperature, the bath temperature was raised to 150° C and the product distilled over a range of 81-82° C. Preparative GC purification afforded pure 1-[perfluorohexyl]ethane. ^{1}H NMR: δ 1.14 (3H, m), 2.10 (2H, m); ^{19}F NMR: ϕ -81.5 (3F, t, $^{3}J_{FF}$ = 9.8 Hz), -117.0 (2F, m), -122.5 (2F, br s), -123.4 (2F, br m), -124.2 (2F, br m), -126.8 (2F, m); HRMS for $C_8H_5F_{13}$: calc. 348.0183, calc. (M-F) 329.0200, found 329.0280.

2-Iodo-1-[perfluorohexyl]-4-phenylbutane. In accordance with a procedure by Oshima,[37] into a 50 mL three-necked round-bottomed flask equipped with argon inlet, rubber septum and stir bar was added 0.5 g (3.78 x 10^{-3} mol) 4-phenyl-1-butene and 2.02 g (4.53 x 10^{-3} mol) perfluorohexyl iodide dissolved in 20 mL of hexanes. 0.4 mL of a 1.0 M solution of triethylborane in hexanes (4 x 10^{-4} mol) was slowly injected through the septum, and the reaction allowed to stir for 6 hours at room temperature. The mixture was washed twice with 10 mL water, the solvent rotary evaporated, and the remaining liquid subject to reduced pressure fractional distillation. A total of 1.81 g (82.8%) of the title compound was collected as a light violet liquid, bp 125-127° C / 1 mm Hg. ^{1}H NMR: δ 2.12 (2H, m), 2.75 (2H, m), 2.92 (2H, m), 4.27 (1H, m), 7.27 (5H, m); ^{19}F NMR: ϕ -81.3 (3F, t, $^{3}J_{FF}$ = 9.8 Hz), -111.8

(1F, dm, $^2J_{FF}$ = 275.9 Hz), -115.2 (1F, dm, $^2J_{FF}$ = 267.3 Hz), -122.3 (2F, br s), -123.3 (2F, s), -124.2 (2F, br s), -126.7 (2F, m); HRMS for $C_{16}H_{12}F_{13}I$: calc. 577.9776, found 577.9815.

1-[Perfluorohexyl]-4-phenylbutane. Into a 50 mL three-necked round-bottomed flask equipped with argon inlet and magnetic stirrer was added 1.5 g (2.59 x 10^{-3} mol) 2-iodo-1-[perfluorohexyl]-4-phenylbutane dissolved in 10 mL DMSO. The bath temperature was raised to 70° C and 0.39 g (1.03 x 10^{-2} mol) sodium borohydride was added in portions to the reaction mixure. Stirring was continued for an additional 6 hours, at which time the mixture was poured into 50 mL of ice water, and carefully acidified with 6 M HCl. 10 mL ether was added, the layers separated, and the aqueous layer extracted with three 10 mL portions of ether. The combined organic layers were washed once with 10 mL 5% aqueous $NaHCO_3$ and twice with 10 mL of water, dried over $MgSO_4$, and the solvent rotary evaporated. Reduced pressure fractional distillation afforded 0.82 g (70.0 %) title compound, bp 83-85° C / 0.25 mm Hg. ^{1}H NMR: δ 1.67 (4H, m), 2.06 (2H, m), 2.64 (2H, t, $^3J_{HH}$ = 6.9 Hz), 7.24 (5H, m); ^{19}F NMR: ϕ -81.4 (3F, t, $^3J_{FF}$ = 9.8 Hz), -114.9 (2F, m), -122.5 (2F, br s), -123.4 (2F, s), -124.1 (2F, s), -126.7 (2F, m); HRMS for $C_{16}H_{13}F_{13}$: calc. 452.0810, found 452.0797.

Competition Kinetics: Hydrogen Atom Abstraction (k_H, Tributyltin Hydride) vs. Addition (k_{add}, Styrene)-General Procedure.

Into each of a set of six Pyrex NMR tubes were added a known amount of C_6D_6, varying, known amounts of styrene and *n*-Bu_3SnH, and a known amount of trifluorotoluene as an internal ^{19}F NMR standard. Each tube was sealed with rubber septa secured with PTFE tape, frozen in a dry ice-isopropanol slush, and subjected to three successive freeze-pump-thaw cycles followed by pressurization with argon. Into each frozen tube was then injected a known amount of the radical precursor (in the case of iodopentafluoroethane, a stock solution in degassed C_6D_6) followed by warming to room temperature (in the case of C_2F_5I, the tubes were flame-sealed before warming) with vigorous shaking. The tubes were then subjected to UV photolysis in a Rayonet reactor until complete consumption of starting material was demonstrated by ^{19}F NMR analysis. Product ratios for varied concentration ratios of nBu_3SnH and styrene allow determination of the ratio k_H / k_{add}. Yields are determined by integration of product resonances versus that of internal standard (ϕ -63.24) in the ^{19}F NMR.

1,1-Difluorohex-1-yl Radical. Ratios of *n*-$R_{HF}H$ / *n*-$R_{HF}CH_2CH_2Ph$ were determined by integration of the -CF_2H and -CF_2- resonances (at ϕ -116.0 and -99.1, respectively) in the ^{19}F NMR.

$R_{HF}X$	[Styrene]	[*n*-Bu_3SnH] / [Styrene]	*n*-$R_{HF}H$ / *n*-$R_{HF}CH_2CH_2Ph$	% Yield
0.094	2.01	0.719	2.30	95
0.094	1.81	0.847	2.73	95
0.094	1.61	1.01	3.26	96
0.094	1.41	1.21	3.93	97
0.094	1.21	1.49	4.88	96
0.094	1.01	1.87	6.21	95

Slope = k_H / k_{add} = 3.39 ± 0.02.

2-[Perfluorohexyl]eth-1-yl Radical. Ratios of n-$R_{HF}H$ / n-$R_{HF}CH_2CH_2Ph$ were determined by integration of the respective -CF_2- resonances at ϕ -117.1 and -115.0.

n-$R_{HF}X$	[Styrene]	[n-Bu_3SnH] / [Styrene]	n-$R_{HF}H$ / n-$R_{HF}CH_2CH_2Ph$	% Yield
0.064	2.96	0.217	3.11	100
0.064	2.83	0.248	3.58	100
0.064	2.69	0.283	4.13	100
0.064	2.56	0.320	4.72	100
0.064	2.42	0.362	5.44	100
0.064	2.29	0.408	6.14	100

Slope = $k_H / k_{add} = 16.0 \pm 0.1$.

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2,2-Difluorohex-1-yl Radical. Ratios of n-$R_{HF}H$ / n-$R_{HF}CH_2CH_2Ph$ were obtained by integration of the respective -CF_2- resonances at ϕ -91.0 and -98.6.

$R_{HF}X$	[Styrene]	[n-Bu_3SnH] / [Styrene]	n-$R_{HF}H$ / n-$R_{HF}CH_2CH_2Ph$	% Yield
0.087	4.08	0.223	5.96	96
0.087	3.97	0.243	6.62	98
0.087	3.85	0.263	7.16	97
0.087	3.73	0.285	7.79	98
0.087	3.62	0.308	8.33	97
0.087	3.50	0.333	9.01	100

Slope = $k_H / k_{add} = 27.3 \pm 0.6$.

1,1,2,2-Tetrafluorohex-1-yl Radical. Ratios of n-$R_{HF}H$ / n-$R_{HF}CH_2CH_2Ph$ were obtained by the sum of integrals of the -CF_2- and -CF_2H resonances of n-R_{HF}-H (at ϕ -117.1 and -136.1, respectively) versus that of the two -CF_2- resonances of n-$R_{HF}CH_2CH_2Ph$ (at ϕ -116.0 and -116.4, respectively.)

n-$R_{HF}X$	[Styrene]	[n-Bu_3SnH] / [Styrene]	n-$R_{HF}H$ / n-$R_{HF}CH_2CH_2Ph$	% Yield
0.085	1.86	0.506	2.33	98
0.085	1.68	0.611	2.90	97
0.085	1.49	0.741	3.56	97
0.085	1.30	0.909	4.30	97
0.085	1.12	1.13	5.34	97
0.085	0.931	1.45	6.65	99

Slope = $k_H / k_{add} = 4.56 \pm 0.10$.

Pentafluoroethyl Radical. Ratios of n-$R_{HF}H$ / n-$R_{HF}CH_2CH_2Ph$ were determined the sum of integrals of the CF_3- and -CF_2H resonances of n-$R_{HF}H$ (at ϕ -86.6 and -138.6, respectively) versus that of the CF_3- and -CF_2- resonances of n-$R_{HF}CH_2CH_2Ph$ (at ϕ -86.1 and -119.2, respectively.)

n-$R_{HF}X$	[Styrene]	[n-Bu_3SnH] / [Styrene]	n-$R_{HF}H$ / n-$R_{HF}CH_2CH_2Ph$	% Yield
0.082	2.20	0.434	1.15	89
0.082	2.08	0.485	1.31	85
0.082	1.96	0.542	1.46	85
0.082	1.84	0.608	1.62	82
0.082	1.71	0.682	1.79	83
0.082	1.59	0.768	2.05	83

Slope = $k_H / k_{add} = 2.62 \pm 0.06$.