Cyclization reactivities of fluorinated hex-5-enyl radicals

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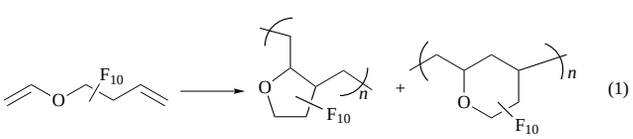
A kinetic study of the effect of fluorine substitution on the rates and regiochemistry of hex-5-enyl radical cyclization is reported. One or more fluorines on or proximate to the double bond of the radical have relatively little electronic effect on either rate or regiochemistry, whereas fluorines substituted at the radical end can have a dramatic impact on both. The relative reactivities of such partially-fluorinated hex-5-enyl radicals can be understood largely in terms of polar effects on the transition state, but radical pyramidalization and, to a lesser extent, addition thermodynamics play a role. The relationship between these fluorine substituent effects and the cyclopolymerizations of fluorinated α,ω-dienes are discussed.

Introduction

Hex-5-enyl radical cyclizations reign supreme in the synthetic chemist's repertoire of methods for making five-membered rings. Elegant physical organic studies, largely by Beckwith and Newcomb, have helped to elucidate the structure–reactivity factors that govern these reactions.[1–5] As is the case for radical–alkene addition reactions in general, the rates of radical cyclization are also determined by a combination of steric, polar and thermodynamic factors which are dependent upon the nature of the substituents that are located both at the radical site and at the alkenyl site.[6,7] In addition, the ability to rationalize the general regioselective preference of 5-*exo versus* 6-*endo* cyclization in such processes using theory has proved to be one of the great successes in the prediction of organic reactivity.[2,8]

Fluorine substituents influence the reactivity of alkyl radicals with respect to alkene additions in a manner which is dependent upon both the degree of fluorination and the proximity of the fluorine substituents to the radical site.[9–12] The high reactivity of perfluoroalkyl radicals derives largely from their great electrophilicity and from the resultant favorable polar transition state for their bimolecular additions to electron-rich alkenes.[9,11,12] In contrast, polar effects appear to be much less important in alkene-addition transition states of partially-fluorinated radicals, where thermodynamic (bond strength) and structural (pyramidal nature) factors have a more significant impact on their only moderately enhanced reactivities.[10]

What about the kinetic effect of fluorine substitution on intramolecular radical cyclizations? This question is significant since it relates to an understanding of fundamental reactivity factors in such cyclizations and how they compare for bimolecular *versus* unimolecular radical–alkene additions. Notably, recent advances in cyclopolymerization technology have demonstrated that fluorinated dienes [*e.g.* reaction (1)] are versatile



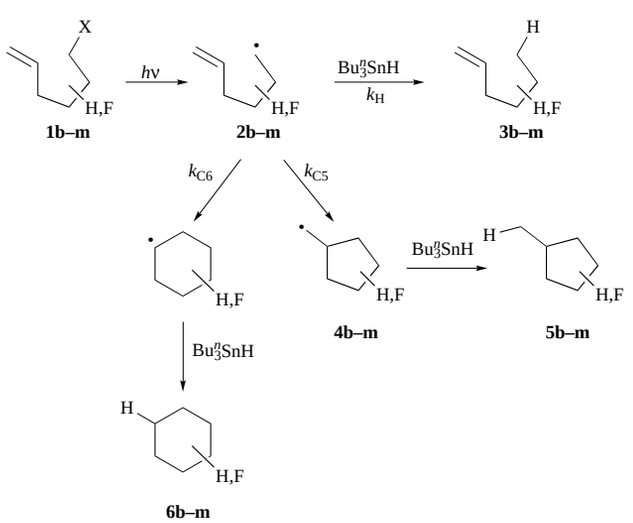
(1)

monomers for generating homopolymers with an unusual combination of properties,[13] and thus there is good reason to decipher the reactivity factors that underlie the scope and utility of these cyclopolymerizations.

In initiating a systematic study of the impact of fluorine substituents on hex-5-enyl cyclizations, we recently reported preliminary results which indicated *inter alia* that polar factors are very important with respect to enhancing cyclization rates.[14,15] Many more systems have now been examined, and a cogent picture of the effect of fluorine substitution on the dynamics of hex-5-enyl radical cyclizations can now be presented, although there remain significant regiochemical questions to be definitively answered.

Results

Absolute rate constants for the cyclizations of the series of fluorinated hex-5-enyl radicals **2b**–**m** (see Table 1) were determined by uni- *vs.* bi-molecular competition experiments as depicted in Scheme 1, under pseudo first-order conditions designed so that kinetically controlled 5-*exo* (and sometimes 6-*endo*) cyclizations of the intermediate radicals took place at a rate competitive with their abstraction of a hydrogen atom from



$$\frac{k_{C5}}{k_H} = \frac{[\mathbf{5}][Bu^n_3SnH]}{[\mathbf{3}]} \quad (2) \qquad \frac{k_{C6}}{k_H} = \frac{[\mathbf{6}][Bu^n_3SnH]}{[\mathbf{3}]} \quad (3)$$

Scheme 1

† Contribution No. 7610.

Table 1 Absolute rate constants for the cyclization of fluorinated hex-5-enyl radicals in C_6D_6 at 30 (±2) °C[a]

	Radical	Structure	k_H/k_{C5}	k_H/k_{C6}	$k_H/10^{-6}$ M^{-1} s^{-1}	$k_{C5}/10^{-6}$ s^{-1}	$k_{C6}/10^{-6}$ s^{-1}
2a	CH_2=$CH(CH_2)_3CH_2^{\bullet}$	—	—	—	0.27[b]	0.005[b]
2b	CH_2=$CF(CH_2)_3CH_2^{\bullet}$	3.64 ± 0.09	—	0.10[c]	0.027 ± 0.006	—
2c	CHF=$CH(CH_2)_3CH_2^{\bullet}$	14.1 ± 0.5	—	2.7[d]	0.19 ± 0.05	—
2d	CF_2=$CH(CH_2)_3CH_2^{\bullet}$	11.7 ± 0.3	—	2.7[d]	0.23 ± 0.02	—
2e	CHF=$CF(CH_2)_3CH_2^{\bullet}$	12.5 ± 0.3	—	2.7[d]	0.22 ± 0.02	—
2f	CF_2=$CF(CH_2)_3CH_2^{\bullet}$	3.9 ± 0.2	—	2.7[d]	0.69 ± 0.06	—
2g	CF_2=$CF(CF_2)_2CH_2CH_2^{\bullet}$	4.5 ± 0.2	—	2.7[d]	0.60 ± 0.05	—
2h	CF_2=$CF(CF_2)_3CF_2^{\bullet}$	1.60 ± 0.02	—	0.75[e]	0.47 ± 0.04	—
2i	CH_2=$CH(CH_2)_3CF_2^{\bullet}$	2.38 ± 0.06	—	9.1[f]	3.8 ± 0.7	—
2j	CH_2=$CH(CH_2)_2CF_2CH_2^{\bullet}$	10.2 ± 0.6	98 ± 9	14[f]	1.4 ± 0.5	0.14 ± 0.05
2k	CH_2=$CH(CH_2)_2CF_2CF_2^{\bullet}$	1.81 ± 0.08	8.0 ± 0.3	21 ± 1[g]	11.6 ± 0.7	2.6 ± 0.2
2l	CH_2=$CHCH_2(CF_2)_2CF_2^{\bullet}$	1.14 ± 0.01	9.1 ± 0.2	51[h]	45 ± 4	5.6 ± 6
2m	CH_2=$CH(CF_2)_3CF_2^{\bullet}$	4.5 ± 0.2	13.0 ± 0.6	51[h]	11.3 ± 1.2	3.9 ± 0.4

[a] Errors are 2σ and have been propagated. [b] Ref. 5. [c] Bu^n_3GeH, ref. 5. [d] Bu^n_3SnH, ref. 5. [e] Et_3SiH, ref. 16. [f] Bu^n_3SnH, ref. 17. [g] $(TMS)_2SiH$ (determined in this work by the usual method).[16] [h] $(TMS)_3SiH$, ref. 16.

Table 2 Relative rates of addition of methyl and trifluoromethyl radicals to some fluoroethylenes[a]

Radical	*CH_2*=CH_2	*CH_2*=CHF	*CHF*=CH_2	*CHF*=CF_2	*CF_2*=CHF
$CH_3^{\bullet}$	(1)	0.9	0.2	1.9	3.9
$CF_3^{\bullet}$	(1)	0.45	0.05	0.033	0.017

[a] Refs. 6 and 19.

a reducing agent. The ratios of products **5**:**3** and **6**:**3** were determined directly by ^{19}F NMR analyses of the respective product mixtures. In determining each rate constant, six values of k_{C5}/k_H and/or k_{C6}/k_H were determined for six different concentrations of reducing agent using eqns. (2) and (3), respectively. These six individual ratios were then averaged in each case to give the value which was used to determine k_{C5} or k_{C6} (see Table 1).

All values of k_H for the various per- and partially-fluorinated radicals, except for that used in determination of the rates of cyclization of **2k**, had been previously determined, and these values are also given in Table 1.[14–17] The value of k_H for the reduction of 1,1,2,2-tetrafluoroalkyl radicals by $(TMS)_3SiH$ was determined in this work, by the usual method,[16] and its value is also given in Table 1. With all required values for k_H being available along with the determined ratios of k_{C5} and k_{C6} to k_H, it was therefore possible to calculate the values for k_{C5} and k_{C6} for each of the hex-5-enyl radical systems, **2b**–**m**. These values are also given in Table 1.

Discussion

The kinetic study of perfluorohex-5-enyl radical system **2h** led to remarkable results in that its rate constant for cyclization, k_{C5}, and its regiochemistry (*i.e.* dominant *exo*-*trig*) were only slightly different from those of the parent hydrocarbon system (k_{rel} = 1.7), with k_{C6} being negligible for both systems. This similarity in reactivities probably derives from a fortuitous cancellation of substituent effects in **2h**. Fluorination increases chain stiffness and creates an unfavorable polarity mismatch between an electrophilic radical and an electron-poor double bond, but this is offset by the significant decrease of π-bond energy in **2h**. The vinyl ether **7** analog cyclizes about seven times faster than

CF_2=$CFOCF_2CF_2CF_2^{\bullet}$ $\quad k_{C5} = 3.5 \times 10^6$ s^{-1}

7

2h, which is consistent with the known lower π-bond energy and higher free-radical reactivity of perfluorovinyl ethers *versus* perfluoroalkenes.[18]

Our study of the series of partially-fluorinated hex-5-enyl radicals has demonstrated the kinetic importance of such polarity factors while providing substantial insight into a number of factors which affect both the rate and the regiochemistry of hex-5-enyl radical cyclizations.

5-*exo*-Cyclization kinetics

Initially it was presumed that a polarity-driven kinetic advantage in hex-5-enyl radical cyclizations would be observed with either a hydrocarbon radical site adding to a fluorinated alkene segment or, *vice versa*, a fluorinated radical site adding to a hydrocarbon alkene segment. In fact, only the latter combination led to a significant cyclization rate enhancement.

Cyclizations involving a hydrocarbon radical adding to a fluorinated alkene. Kinetic data for radicals **2b**–**f**, all of which involve hex-5-enyl radical cyclizations of a primary hydrocarbon radical site onto a fluorinated alkene segment, indicate that the degree of fluorination of the double bond has little impact upon the rate of cyclization. Only the 5-fluoro-, **2b**, and the tri- and penta-fluoro systems, **2f** and **g**, exhibit any significant deviation from the cyclization rate of the parent system, with the first being significantly lower, and the latter two being slightly enhanced.

Such a small kinetic effect of olefinic fluorine substituents on alkyl radical addition reactions is consistent with Tedder and co-workers' early studies on methyl affinities (Table 2), where the range of reactivities for the addition of a methyl radical to ethylenes with varying fluorine content is also relatively small.[6,19]

A single fluorine substituent at C-5 (as in radical **2b**) causes a significant, 10-fold decrease in rate constant. This decrease no doubt derives largely from the steric/electrostatic influence of the 5-fluoro substituent, an effect which would be expected from virtually any substituent at the 5-position. A methyl substituent, for example, gives rise to a 45-fold decrease in cyclization rate.[20] Interestingly, whereas the presence of a 5-methyl substituent causes *endo*-cyclization to become preferred (63%), the cyclization of the 5-fluorohex-5-enyl radical remains *exo*-specific within our NMR analytical uncertainty (±4%).

A small overall enhancement in reactivity (2.5-fold) is observed in the cyclization of the 5,6,6-trifluorohex-5-enyl radical (**2f**). The π-bond of **2f** thus is at least reactive enough [consider that the heat of hydrogenation of trifluoroethene (−45.7 kcal mol^{-1}) is 13 kcal mol^{-1} greater than that of ethylene[21]] to overcome the steric inhibition of its 5-fluoro substituent. Polar influences, although possibly of some minor importance in the cases of **2f** and **g**, should not play a significant role in any of these cyclizations, since the reported electron affinities (E_{ea}) of ethylene (−1.78 eV), fluoroethene (−2.39 eV), (*Z*)- and (*E*)-1,2-difluoroethene (−2.18 and −1.84 eV) and 1,2,2-tri-

fluoroethene (−2.45 eV) encompass a total range of only 0.7 eV.[22] In the olefin addition reactions of the more nucleophilic *tert*-butyl radical, Fischer observed a rate variation of *ca.* 5 for olefins with a 0.7 eV difference in electron affinity.[23] Therefore polar influences should not be very significant for cyclizations of **2b**–**f**.

The reactivities of vinyl fluorine-substituted radicals **2c**–**e** can be effectively rationalized in terms of combinations of modest steric and enthalpic effects. The lack of significant influence of single or geminal fluorine substituents at the 6-position, or of vicinal 5,6-difluoro substituents, probably derives from a canceling out of advantageous and disadvantageous effects in each case. The single 6-fluoro substituent should stabilize, by approximately the same amount, both the olefin[24] and the radical which results from cyclization;[12,25] hence, no resultant net effect. Geminal 6,6-difluoro substituents appear to slightly stabilize the π-system, based upon the 3.7 kcal mol^{-1} greater π-bond dissociation energy ($D_\pi°$) of $CH_2{=}CF_2$ than that of ethylene.[12] With the stability of the resultant radical from cyclization being essentially unaffected by the presence of the geminal fluorine substituents, there should be little effect on the cyclization rate constant by 6,6-difluoro substitution. Thermodynamic data indicate that vicinal fluorination, such as in the 5,6-difluoro system **2e**, destablilizes the π-system by *ca.* 5 kcal mol^{-1}.[21] This, combined with the small stabilization of the cyclized radical, are apparently enough to offset the steric inhibition of the 5-fluoro substituent to give the observed kinetic result.

To us, the most surprising result was that the 3,3,4,4,5,6,6-heptafluorohex-5-enyl radical, **2g**, exhibits very little rate enhancement relative to the hydrocarbon parent ($k_{rel} = 2.2$), and its rate constant is only slightly greater than that of the perfluoro radical, **2h**. A recent study of the reactivity of $R_FCH_2CH_2^{\bullet}$-type radicals demonstrated that such radicals do not exhibit electrophilic character in their additions to alkenes.[10] They are π-radicals with a reactivity profile much like that of an *n*-alkyl radical. Thus one might have expected to derive more than the observed kinetic advantage from the advantageous polar transition state involving an alkyl radical adding to a fluorinated alkene. As the data in Table 2 indicate, however, there is apparently significantly less kinetic advantage to be derived from such an addition than for the addition of a fluorinated radical to a hydrocarbon alkene.

What the above results for radicals **2b**–**g** indicate is that, for various reasons, hex-5-enyl radical cyclizations which involve an alkyl radical cyclizing onto a fluorinated alkene site occur with relatively little impact on rate.

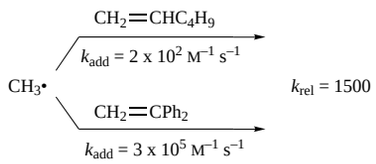
Cyclizations involving a fluorinated radical adding to a hydrocarbon alkene. In contrast, when the mode of substitution is reversed, that is when the radical is fluorinated and the alkene fragment is not (radicals **2i**, **k**, **l** and **m**) a much greater impact on reactivity is observed.

The overall reactivities of these radicals in their unimolecular hex-5-enyl cyclization processes reflect those same factors which affect the reactivity of partially-fluorinated radicals in their bimolecular addition reactions with alkenes, such as styrene. The data in Table 3 indicate this clearly, and they also reflect the general leveling effect which would be expected for the more facile unimolecular cyclization processes which have log *A* values about 1–2 units larger than those for the bimolecular additions.

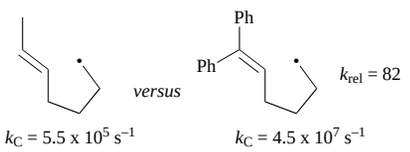
Such a leveling effect can also be seen to operate well in non-fluorinated systems, as shown in Scheme 2.[5,26,27]

Our earlier studies of the bimolecular alkene addition reactivity of α,α-difluoro alkyl radicals indicated that they exhibited little 'philicity', reacting with styrene and pentafluorostyrene (E_i values of 8.43 and 9.20 eV, respectively) at virtually the same rate.[10] The significantly greater reactivity of α,α-difluoroalkyl radicals in bimolecular additions, hydrogen-abstraction reactions and unimolecular cyclizations can be largely attributed to the pyramidal nature of their radical sites.[28,29]

Bimolecular addition:



Unimolecular cyclization:



Scheme 2

Table 3 Comparison of the effect of degree of fluorine substitution on rate constants for cyclization *versus* rate constants for addition of styrene at 30 (±2) °C

Addition to styrene[9,17]			Hex-5-enyl cyclization		
Radical	$k_{add}/10^{-5}$ M^{-1} s^{-1}	k_{rel}	k_{rel}	$k_{C5}/10^{-5}$ s^{-1}	Radical
$RCH_2CH_2^{\bullet}$	1.2[a]	(1)	(1)	2.7[b]	**2a**
$RCH_2CF_2^{\bullet}$	27	22.5	14	38	**2i**
$RCF_2CH_2^{\bullet}$	5.2	4.3	5.2	14	**2j**
$RCF_2CF_2^{\bullet}$	200	167	43	116	**2k**
n-$R_F^{\bullet}$	460	383	166	450	**2l**
n-$R_F^{\bullet}$	460	383	42	113	**2m**

[a] From A. Citterio, A. Arnoldi and F. Minisci, *J. Org. Chem.*, 1979, **44**, 2674, as modified for temperature and other factors in Table III of L. J. Johnston, J. C. Scaiano and K. U. Ingold, *J. Am. Chem. Soc.*, 1984, **106**, 4877. [b] C. Chatgilialoglu, K. U. Ingold and J. C. Scaiano, *J. Am. Chem. Soc.*, 1981, **103**, 7739.

Since two α-fluorine substituents are sufficient to induce significant non-planarity in a radical, the resultant σ-radicals should have an inherent energetic advantage in alkene addition reactions over planar alkyl radicals, including β- and γ-fluorine substituted *n*-alkyl radicals.[30–32] Such α,α-difluoroalkyl radicals are sufficiently non-planar at their radical centers that little or no further bending should be required in the transition states for their additions to alkenes.[33] Such factors are probably sufficient to explain the 13-fold rate enhancement for cyclization of α,α-difluorohex-5-enyl radical **2i**.

However, thermodynamic factors may affect the reactivity of such radicals to some degree, since, according to the calculated C–C bond dissociation energies in Table 4,[17] the $\Delta H°$ value for their C–C bond formation should be significantly more exothermic. Nevertheless, since radical additions to double bonds involve early transition states, the overall enthalpies of reaction should be relatively unimportant. Indeed, we have demonstrated this to be the case in our studies of the alkene addition reactivities of perfluoro-*n*-alkyl radicals.[9]

The slight rate enhancement observed for cyclization of radical **2j** is consistent with the slight electrophilicity of such radicals which was demonstrated earlier in our studies of their bimolecular olefin addition reactivity.[10] The similar reactivities of **2j** and hydrocarbon parent **2a** are consistent with the similarity of the EPR parameters for these two types of radicals.[37] That is, they are both effectively planar π-radicals.

The α,α,β,β-tetrafluorohex-5-enyl radical, **2k**, ($k_{rel} = 43$) of course, retains the reactivity which comes from its σ-nature, but also gets a significant boost in reactivity from its substantial electrophilic character. Although laser flash photolysis (LFP) data are limited, the rate constant for addition of

Table 4 Calculated C–C bond dissociation energies [B3LYP/6-31G(d)]

C–C Bond	D_o[a]/kcal mol^{-1} Expt.	Lit.
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) using 0.9806 ZPE and a temperature correction of $4RT$. [b] Ref. 34. [c] Ref. 35. [d] Ref. 36.

Table 5 Ionization energies, electron affinities and absolute electronegativities of some fluorinated alkyl radicals[38]

Radical	E_i/eV Calc.	Lit.[39]	E_{ea}/eV Calc.	Lit.[40]	χ/eV Calc.	Lit.
$CH_3^{\bullet}$		9.84		0.08		4.96
$CH_3CH_2CH_2^{\bullet}$		8.09		−0.07		4.01
$(CH_3)_2CH^{\bullet}$		7.37		−0.32		3.53
$(CH_3)_3C^{\bullet}$		6.70		−0.16		3.27
$CF_3^{\bullet}$	9.05	9.05	1.97	1.84	5.51	5.45
$CH_3CF_2^{\bullet}$	7.66	7.92	0.84		4.25	
$CHF_2CF_2^{\bullet}$	8.88	9.29				
$CF_3CF_2^{\bullet}$	9.26	9.98	2.09	1.81	5.67	5.90
$CF_3CF_2CF_2^{\bullet}$	9.66	10.06	2.21	>2.65	5.94	6.36
$CF_3(CF_2)_2CF_2^{\bullet}$	9.11		2.27		5.69	
$(CF_3)_2CF^{\bullet}$	9.98	10.50	2.80	>2.65	6.39	6.58
$(CF_3)_3C^{\bullet}$			3.72	3.4	(7.4)	

$CH_3CH_2CF_2CF_2^{\bullet}$ to styrene (k_{rel} = 167, relative to *n*-alkyl) indicates a substantial enhancement compared to an α,α-difluoroalkyl radical.[17] Its rate of H-abstraction from Bu^n_3SnH (k_{rel} = 38, compared to *n*-alkyl) also reflects the very favorable matchup of transition state polarities which is characteristic of highly fluorinated radicals.[17] Lastly, the sparse ionization potential data which are available for such radicals (see Table 5, $HCF_2CF_2^{\bullet}$) also reflect a significant electrophilicity, approaching but not equal to that of perfluoroalkyl radicals.

In the system with three CF_2 groups, *i.e.* **2l**, the radical takes on perfluoroalkyl character and the impact on the cyclization rate is magnified still further. The dominant factor which has been credited for giving rise to the high reactivities of perfluoro-*n*-alkyl radicals in their additions to alkenes, particularly to electron-rich alkenes, is their high electrophilicities (again see Table 5). 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 barriers to reaction.

The large rate enhancement (k_{rel} = 166) observed for cyclization of **2l** is consistent with the 30 000-fold polarity-driven rate ratio for n-$C_3F_7^{\bullet}$ *versus* $RCH_2CH_2^{\bullet}$ addition to hex-1-ene.[9] Nevertheless, system **2l** is still not ideal in terms of transition state polarity matchup because the proximity of the perfluoroalkyl group to the olefinic segment will serve to diminish its nucleophilicity significantly [see reaction (4)].

$$n\text{-}C_7F_{15}^{\bullet} + CH_2{=}CHCH_2(CF_2)_2CF_3 \qquad k_{rel} \approx 0.1 \text{ (relative to hex-1-ene)}^{41} \quad (4)$$

The reactivity of the octafluorohex-5-enyl radical system **2m** (k_{rel} = 42) is diminished relative to that of the hexafluoro system **2l**. This can be attributed, at least in part, to the impact of the perfluoroalkyl group on the nucleophilicity of the terminal alkene segment [reaction (5)], which will serve to further

$$n\text{-}C_7F_{15}^{\bullet} + CH_2{=}CH(CF_2)_3CF_3 \qquad k_{rel} \approx 0.03 \text{ (relative to hex-1-ene)}^{41} \quad (5)$$

diminish the nucleophilicity of the terminal double bond of **2m**, and hence make it less reactive with its highly fluorinated radical terminus.

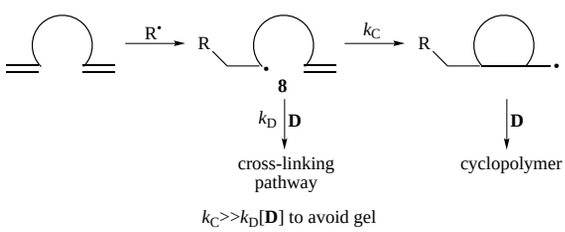
Table 6 Regioselectivity of fluorinated hex-5-enyl radical cyclizations at 30 °C

Radical	*endo*-Selectivity (%) Observed	Predicted[43]
$CH_2{=}CHCH_2CH_2CF_2CF_2^{\bullet}$ (**2k**)	18.3	15.6
$CH_2{=}CHCH_2CF_2CF_2CF_2^{\bullet}$ (**2l**)	11.1	5.7
$CH_2{=}CHCF_2CF_2CF_2CF_2^{\bullet}$ (**2m**)	25.7	24.2
$CH_2{=}CHCH_2CH_2CF_2CH_2^{\bullet}$	9.1	8.9
2a–**2i**	<4	<4

Regiochemistry. Whereas cyclizations of parent hydrocarbon, perfluoro- and most of the partially-fluorinated hex-5-enyl radical systems occur with the expected dominant *exo*-selectivity, radicals **2k**, **l**, **m** (and even **j**) exhibit a surprising degree of 6-*endo* cyclization (Table 6).[42] The 25.7% *endo* cyclization exhibited by **2m**, for example, means that this cyclization proceeds 780 times faster than the *endo* cyclization of the parent radical **2a**.

Although we do not have a good explanation for the regiochemical diversity exhibited by these radicals in their cyclizations, it was predicted computationally (Table 6).[43] A complete description of these computational results will be published after further analysis, which may offer some rationalization for the experimentally-observed enhanced *endo* reactivity of these four radicals.

Applications. Soluble, amorphous perfluoroplastics with outstanding chemical, thermal and electrical properties were first commercialized by DuPont and Asahi Glass in the late 1980s.[13] A characteristic structural feature of all of these polymers is the presence of a five- or six-membered ring in each repeating unit. Whereas DuPont's Teflon® AF product is a family of copolymers of 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole with tetrafluoroethylene, Asahi Glass' polymers are based on free radical cyclopolymerization of $CF_2{=}CFO(CF_2)_nCF{=}CF_2$ (n = 1,2) monomers. A wide variety of related α,ω-unsaturated monomers have been studied by Asahi Glass, DuPont, Daikin and other industries in search of polymers with superior properties, although the regioselectivity of cyclopolymerization toward four-, five- or six-membered ring formation remains uncertain in many cases. Moreover, undesirable gellation (cross-linking) can compete with cyclopolymerization, and to avoid cross-linking it is necessary to maximize the rate of cyclization of the unsaturated radical **8** generated during polymerization (Scheme 3).

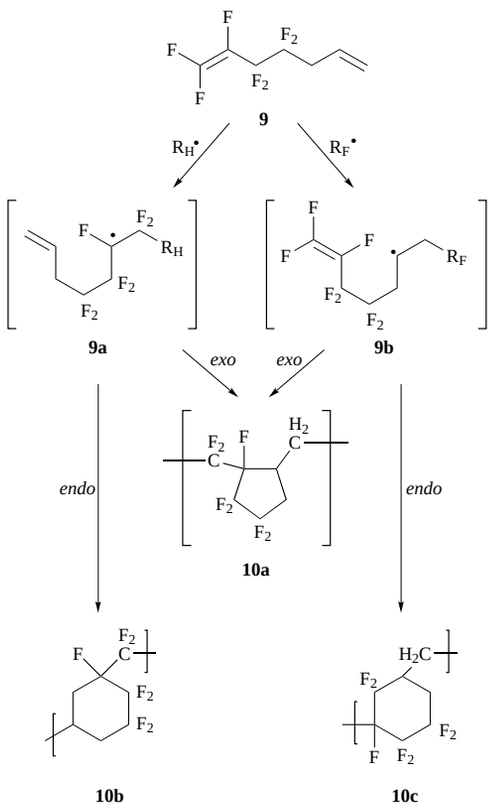


Scheme 3 Cyclopolymer *vs.* gel formation

The results of our systematic study of fluorine substituent effects on the rates and regiochemistry of hex-5-enyl radical cyclizations provides considerable insight into the design of

fluorinated dienes that will cyclopolymerize with maximum efficiency upon free-radical initiation. Some preliminary findings with 1,1,2,3,3,4,4-heptafluorohepta-1,6-diene (**9**)[44] are discussed below to illustrate the various factors potentially important to these free-radical cyclopolymerizations.

The kinetic results above imply that α,ω-dienes with one electron-rich double bond (non-fluorinated) and one electron-deficient double bond (fluorinated) are required to maximize the rate of cyclopolymerization. A perhaps less obvious and more interesting prediction is that the nature of the free-radical initiator (*i.e.* is electrophilicity) could control both the cyclization rate and primary structure of the resulting cyclopolymer. For example, initiation of **9** by a perfluoroalkyl radical should preferentially give **9b** *vs.* **9a** from an initiating alkyl radical, and based on the model cyclization kinetics (*cf.* **2l** *vs.* **2g**, Table 1), *exo* cyclization *via* **9a** ought to be about an order of magnitude faster than cyclization *via* **9b** (Scheme 4). Moreover, the model



Scheme 4 Cyclopolymerization of diene **9**

regioselectivity results (Table 6) predict that the polymer from an alkyl radical initiator should contain not only a different six-membered ring (**10b** *vs.* **10c**) but also about three times more six-membered ring in the cyclopolymer[45] (*exo*-cyclization of **9a** or **9b** give the same five-membered ring repeat unit in the polymer, **10a**).

The diene **9** is a much more reactive monomer than perfluorohepta-1,6-diene or hexa-1,5-diene. Unlike the perfluorodienes, **9** slowly polymerizes without an added initiator to a white solid upon storage at room temperature for about a week. It homopolymerizes at 40 °C either neat or in CFC-113 when initiated with 1 mol% bis(perfluoropropionyl) peroxide (**3P**). No double bonds were detected in the polymer by IR analysis. Unfortunately, the polymer (T_g 106–113, T_m 258–260 °C by DSC, second heat) was not soluble in organic solvents so it could not be fully characterized, but a high temperature ^{19}F NMR spectrum could be acquired for the melt. No vinyl fluorines were present and only saturated fluorine resonances appeared as multiplets at δ −103.5–130.6, a singlet at δ −163.5, a broad multiplet at δ −181.0 and a singlet at δ −187.7. The latter two (1 : 4.7 ratio) are consistent with methine fluorines in a six-membered ring,[46] but it was not possible to distinguish among structures **10b**, **10c**, or *cis*, *trans*-isomers by ^{19}F NMR spectroscopy. The δ −163.5 resonance is assigned to the methine fluorine in **10a**,[47] and integration of the methine fluorine resonances indicates the ratio of five- to six-membered rings in the polymer is nearly 1 : 1. This is at variance with the predictions from the model hex-5-enyl radical cyclizations.[45] Moreover, when AIBN or $(Me_2CHCOO)_2$ were used as initiators (at 60–70 °C), the resulting polymers were essentially identical by NMR spectroscopy to that obtained by **3P** initiation. The provocative prediction that cyclopolymer ring structure can vary depending on the choice of free-radical initiator requires more research.[48] We plan to continue our experimental and theoretical studies on fluorinated radical cyclizations and their related diene cyclopolymerizations.

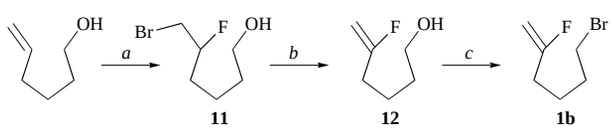
Experimental

General

^{1}H, ^{13}C and ^{19}F NMR spectra (300, 75 and 282 MHz, respectively) were measured in $CDCl_3$ using TMS as internal standard for ^{1}H and ^{13}C spectra, and $CFCl_3$ for ^{19}F spectra. *J* values are given in Hz. All reagents, unless otherwise specified, were purchased from Aldrich, Fisher, PCR or Acros, and were used as received. Dichloromethane was distilled from calcium hydride and used immediately. Diethyl ether was distilled from sodium benzophenone ketyl and used immediately. Dimethylformamide, dimethyl sulfoxide and acetonitrile were commercial anhydrous grade. Preparative gas chromatography was carried out on a 20 ft × 0.25 in copper column packed with 20% SE-30 on Chromosorb P. All reactions, unless otherwise specified, were performed under an argon atmosphere.

Synthesis of 2-fluoro-6-bromohex-1-ene (1b)

6-Bromo-5-fluorohexanol (11). 1.4 g (0.014 mol) of hex-5-enol (Aldrich) was mixed with 3.0 g of *N*-bromosuccinimide in 10 ml methylene chloride in a polyethylene container at room temp. 1.4 ml (0.042 mol) of HF–pyridine (70% HF in pyridine) was slowly added to the mixture at room temp., and then stirred for 2 h (Scheme 5).[49] The reaction mixture was poured into 100 ml



Scheme 5 *Reagents and conditions:* (*a*) HF–pyridine, CH_2Cl_2, room temp.; (*b*) Na–*tert*-butyl alcohol, 50 °C; (*c*) TsCl–pyridine, 0 °C, and then LiBr–DMF, room temp.

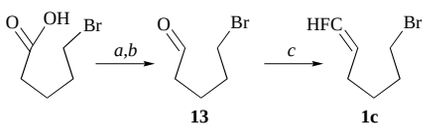
of saturated $NaHCO_3$ solution and extracted with $CHCl_3$ (3 × 100 ml). The dark red mixture was distilled under reduced pressure (0.5 mmHg, 70 °C) to obtain 2.8 g (45% yield) of 6-bromo-5-fluorohexan-1-ol (**11**), which was immediately used in the next step.

2-Fluoro-6-bromohex-1-ene (1b). Sodium metal (5 equiv.) was added to *tert*-butyl alcohol in a round-bottom flask and stirred until the sodium had completely dissolved. At 50 °C, 2.8 g (6.3 mmol) of 6-bromo-5-fluorohexanol (**11**) was added through a syringe. After stirring for about 0.5 h at 50 °C, the mixture was distilled under reduced pressure (0.5 mmHg, 50 °C) to remove *tert*-butyl alcohol. To the residue 50 ml of saturated $NaHCO_3$ was added and extracted by diethyl ether (3 × 50 ml). Then, 2-fluoro-6-hydroxyhex-1-ene (**12**) was obtained (Scheme 5), which was converted through tosylation (TsCl–pyridine) and bromination (LiBr–DMF) to the title compound. The final purification by column chromatography gave **1b**, δ_H 1.70 (m, 2H), 1.93 (m, 2H), 2.24 (m, 2H), 3.44 (t, *J* 7, 2H), 4.26 (m of d, *J* 51, 1H), 4.54 (d of d, *J* 18, 3, 1H); δ_C 24.5, 30.7, 31.1, 31.7, 33.17, 90.0 (d); δ_F −95.39 (q of d, *J* 51, 17, 1F); (Calc. for $C_6H_{10}BrF$: 179.9950. Found: 179.9950).

2-Fluorohex-1-ene (3b)
Reduced compound (**3b**) was obtained by reduction of **1b** by Bu_3SnH under photolytic conditions. 0.067 g of **1b** was mixed with 1.1 equiv. of the tin hydride in 0.4 ml of C_6H_6 and sealed in a Pyrex NMR tube. The reaction mixture was photolyzed in a Rayonet reactor for 12 h, and was distilled under reduced pressure (0.5 mmHg, room temp.) to remove tin compounds. Further purification by preparative GC gave **3b**, δ_H 0.93 (t, *J* 7, 3H), 1.36 (m, 2H), 1.48 (m, 2H), 2.18 (m, 2H), 4.20 (m of d, *J* 51, 1H), 4.48 (d of d, *J* 18, 3, 1H); δ_C 13.7, 22.0, 28.1, 31.34, 31.7, 89.2 (d); δ_F −95.13 (q of d, *J* 51, 17, 1F); (Calc. for $C_6H_{11}F$: 102.0845. Found: 102.0861).

1-Fluoro-1-methylcyclopentane (5b)
5b was obtained by cyclization of **1b** under photolytic conditions using Bu_3GeH as the radical initiator. 0.067 g of **1b** was mixed with 1.1 equiv. of the Bu_3GeH in 0.4 ml of C_6H_6 and sealed in a Pyrex NMR tube. The reaction mixture was photolyzed in a Rayonet reactor for 12 h, and was distilled under reduced pressure (0.5 mmHg, room temp.) to separate **5b** and C_6H_6 from the reaction mixture. Further purification by preparative GC gave **5b**, δ_H 1.29 (d, *J* 20.6, 3H), 1.16–1.42 (m, 4H), 1.76–1.97 (m, 4H); δ_F −134.66 (m, 1F); (Calc. for $C_6H_{11}F$: 102.0845. Found: 102.0860).

Synthesis of 1-fluoro-6-bromohex-1-ene (1c)
5-Bromopentanal (13). 10.8 g (60 mmol) of 5-bromopentanoic acid and 75 ml of diethyl ether were mixed in a dry 250 ml round-bottom flask under nitrogen (Scheme 6). The



Scheme 6 *Reagents and conditions:* (*a*) $BH_3{\cdot}Me_2S$, Et_2O, room temp.; (*b*) PCC, CH_2Cl_2, reflux; (*c*) Bu_3P–$CFCl_3$, CH_2Cl_2, 0 °C

mixture was stirred vigorously and borane–dimethyl sulfide (BMS) (Aldrich; 6.1 ml, 60 mmol) was added dropwise using a syringe.[50] Following the addition of the initial 2–3 ml of BMS, when the gas evolution had ceased, the mixture was heated under gentle reflux to complete the evolution of gas (hydrogen). The remainder of the BMS was added at such a rate as to maintain a gentle reflux. After the addition, the mixture was heated under reflux for 2 h. The solvent and dimethyl sulfide were removed under vacuum and 20 ml of methylene chloride was introduced to dilute the product. This solution was added dropwise to a well-stirred suspension of PCC (14.3 g, 66 mmol, Aldrich) in 100 ml of methylene chloride in a 500 ml flask. The stirred mixture was heated under reflux for 1 h and then diluted with 150 ml of diethyl ether. The supernatant liquid was filtered and dried over $MgSO_4$. The colorless filtrate was concentrated and distilled under reduced pressure to give 5-bromopentanal (**13**), yield 6.8 g (70%), δ_H 1.84 (m, 4H), 2.51 (t, 2H), 3.43 (t, *J* 7, 2H), 9.78 (t, 1H); δ_C 20.3, 31.6, 32.9, 42.4, 183.2.

1-Fluoro-6-bromohex-1-ene (1c). A 300 ml three-necked flask was charged with 22.4 ml (0.090 mol) of tri-*n*-butylphosphine and 30 ml of methylene chloride.[51] The solution was cooled in an ice bath, and 2.8 ml (0.030 ml) of trichlorofluoromethane was added *via* a syringe. The resultant mixture was stirred at 0 °C for 1 h and then at room temp. for 6 h. To this mixture was added 3.9 g (0.024 mol) of 5-bromopentanal (**13**) *via* syringe. The reaction was stirred for 8 h at room temp. 40 ml of 10% NaOH was added slowly to the reaction mixture followed by stirring at room temp. for 18 h. The resultant organic layer was acidified and then was extracted with methylene chloride (2 × 50 ml), followed by washing with 40% sodium bisulfite (2 × 50 ml) and water (2 × 50 ml), and the organic portion dried with magnesium sulfate. Purification was by reduced pressure distillation (60 °C, 0.5 mmHg) to give 1.3 g (30% yield) of **1c** (major isomer was *Z*, >98%), δ_H 1.14 (m, 2H), 1.35 (m, 2H), 1.86 (q, 2H), 3.04 (t, *J* 7, 2H), 4.25 (m of d, *J* 43, 1H), 6.11 (d of d, *J* 85, 5, 1H); δ_C 24.5, 30.7, 32.1, 32.7, 33.5, 90.2 (d); δ_F −130.44 (q, *J* 43, 1F); (Calc. for $C_6H_{10}BrF$: 179.9950. Found: 179.9927).

1-Fluorohex-1-ene (3c)
Compound **3c** was obtained by reduction of **1c** by tributyltin hydride under photolytic conditions. 0.1 g (0.6 mmol) of **1c** was mixed with the tributyltin hydride in 0.3 ml of pentane and sealed in a Pyrex NMR tube. The mixture was photolyzed in a Rayonet reactor for 12 h. Both reduced product **3c** and cyclized product **5c** were obtained (about 50 : 50). The reaction mixture was distilled under reduced pressure (0.5 mmHg, room temp.) to separate the tin compounds from the products. Further purification of both **3c** and **5c** was by preparative GC. Note that the double bond was isomerized to give both *Z* and *E* isomers of **3c**.

(*Z*)-1-Fluorohex-1-ene [(*Z*)-3c]. δ_H 0.82 (t, *J* 7, 3H), 1.20 (m, 4H), 2.05 (q, 2H), 4.46 (m of d, *J* 43, 1H), 6.19 (m of d, *J* 85, 1H); δ_F −130.92 (q, *J* 43, 1F); (Calc. for $C_6H_{11}F$: 102.0845. Found: 102.0861).

(*E*)-1-Fluorohex-1-ene [(*E*)-3c]. δ_H 0.81 (t, *J* 7, 3H), 1.11 (m, 4H), 1.59 (q, 2H), 5.21 (m, 1H), 6.25 (d of d, *J* 85, 12, 1H); δ_F −130.34 (d of d, *J* 85, 19, 1F); (Calc. for $C_6H_{11}F$: 102.0845. Found: 102.0868).

(Fluoromethyl)cyclopentane (5c)
Cyclized compound **5c** from **1c** was isolated from the reaction mixture as described above in preparing **3c**, by preparative GC, δ_H 1.32–1.42 (m, 4H), 1.5–1.58 (m, 4H), 3.04 (m, 1H), 3.99 (d of d, *J* 48, 7, 2H); δ_F −215.9 (d of t, *J* 48, 17, 1F); (Calc. for $C_6H_{11}F$: 102.0845. Found: 102.0843).

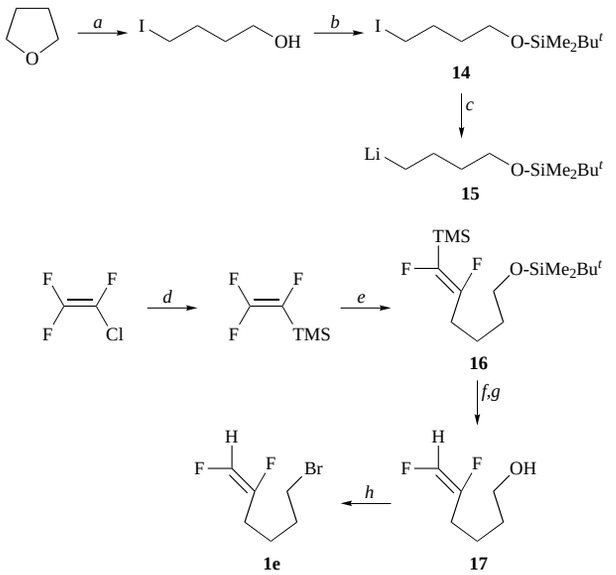
1,1-Difluoro-6-bromohex-1-ene (1d)
To a dry 300 ml three-necked flask under nitrogen were added 100 ml of THF and 4.2 g (0.02 mol, 3.6 ml) of dibromodifluoromethane and the mixture was then cooled to 0 °C. 13.2 g (0.04 mol) of $P[N(CH_3)_2]_3$ was dissolved in 15 ml of THF and added dropwise to the mixture.[52] The resultant suspension of white solid was stirred at 0 °C for 1 h, and 3.3 g (0.02 mol) of 5-bromopentanal (**13**) dissolved in 20 ml of THF was added dropwise *via* a syringe. The mixture was stirred at 0 °C for 0.5 h and warmed to 45 °C for 2 h. To the resultant mixture was added 10 ml of water to stop the reaction. The organic portion was concentrated by rotary evaporator to get rid of the THF. The residue was dissolved in 150 ml of diethyl ether and washed with water (2 × 100 ml), and then dried over $MgSO_4$. Purification was by column chromatography yielding 2.8 g (71% yield) of **1d**, δ_H 1.56 (m, 2H), 1.90 (m, 2H), 2.03 (m, 2H), 3.43 (t, *J* 7, 2H), 4.14 (m of d, *J* 25, 1H); δ_C 21.9, 27.4, 28.5, 32.4, 33.5, 156.3 (t); δ_F −89.38 (d, *J* 47, 1F), −91.85 (q, *J* 25, 1F); (Calc. for $C_6H_9BrF_2$: 197.9856. Found: 197.9834).

1,1-Difluorohex-1-ene (3d) and difluoromethylcyclopentane (5d)
The procedure for making these two compounds from **1d** was the same as that used in making **3c** and **5c** from **1c**.

1,1-Difluorohex-1-ene (3d). δ_H 0.91 (t, *J* 7, 3H), 1.35 (m, 4H), 1.97 (m, 2H), 4.13 (d of t, *J* 25, 3, 1H); δ_F −90.41 (d, *J* 50, 1F), −92.83 (q, *J* 24, 1F); (Calc. for $C_6H_{10}F_2$: 120.0751. Found: 120.0739).

(Difluoromethyl)cyclopentane (5d). δ_H 1.53–1.66 (m, 6H), 1.76–1.82 (m, 2H), 2.36 (m, 1H), 5.66 (d of t, *J* 57, 5, 1H); δ_F −119.44 (d of d, *J* 57, 15, 2F);[5–8] (Calc. for $C_6H_{10}F_2$: 120.0751. Found: 120.0713).

Synthesis of 1,2-difluoro-6-bromohex-1-ene (1e)
Part A: 4-(*tert*-butyldimethylsiloxy)butyllithium (15). The lithium compound was prepared by adaptation of pro-



Scheme 7 *Reagents and conditions:* (*a*) Me_3SiI, room temp.; (*b*) $Me_2Si(Bu^t)Cl$–imidazole, DMF; (*c*) Bu^tLi, THF, −78 °C; (*d*) Bu^tLi–Me_3SiCl, pentane, −110 °C, then warm; (*e*) **15** in Et_2O and pentane, −78 °C; (*f*) KF, DMF–H_2O, room temp.; (*g*) Bu_4NF, THF, room temp.; (*h*) TsCl, pyridine, 0 °C, then LiBr–DMF, room temp.

cedures.[53–55] To a dry 250 ml round-bottom flask was added 50 ml of dry THF, and then 10 g (0.050 mol) of trimethylsilyl iodide was syringed into the THF under nitrogen. The mixture was stirred for 1 h at room temp. before the excess THF was removed by a rotary evaporator. The residue was diluted with diethyl ether (200 ml) and washed with saturated $NaHCO_3$ solution (2 × 150 ml). The organic layer was dried over $MgSO_4$, and then diethyl ether was evaporated. To the residue in a 300 ml round-bottom flask were added about 2 equiv. (15.5 g, 0.10 mol) of dimethyl-*tert*-butylsilyl chloride and 4 equiv. (14.5 g, 0.20 mol) of imidazole in 60 ml of DMF. After stirring for 48 h at room temp., the mixture was poured into 200 ml of diethyl ether, and then the mixture was extracted with H_2O (3 × 100 ml) and dried over $MgSO_4$. The resulting solution was distilled under reduced pressure to give 12.5 g of *tert*-butyldimethylsilyl 4-iodobutyl ether (**14**) (79% yield), δ_H 0.20 (s, 6H), 1.04 (s, 9H), 1.82 (m, 2H), 2.02 (m, 2H), 3.71 (t, *J* 7, 2H), 3.79 (t, *J* 7, 2H). To a dry 500 ml round-bottom flask under argon were added 10 g (0.032 mol) of **14**, dry 120 ml pentane, and 80 ml diethyl ether. The solution was cooled to −78 °C, the stirrer started, and 42 ml (0.070 mol, 1.7 M in pentane, Aldrich) of Bu^tLi in pentane was then added dropwise *via* a syringe. Stirring was continued at −78 °C for an additional 5 min following the addition, the cooling bath was then removed, and the mixture was allowed to warm and stand at room temp. for 2 h to consume unreacted Bu^tLi. The solution (200 ml, approx. 0.16 M of **15**) was used at once in Part B.

Part B: *tert*-butyldimethylsilyl 5,6-difluoro-6-trimethylsilylhex-5-enyl ether (16). Compound **16** was prepared by an adaptation of procedures.[56,57] To 60 ml of diethyl ether in a 300 ml flask cooled to −110 °C was transferred 10 g (0.086 mol) of chlorotrifluoroethylene, and then 45 ml (0.078 mol, 1.7 M in pentane, Aldrich) of Bu^tLi was added dropwise. The mixture was stirred at −110 °C for 0.5 h before the temperature was allowed to rise to −60 °C. To the mixture was added 10 g of trimethylsilylchloride and the mixture was stirred for 0.5 h. After warming up to 0 °C and remaining at that temperature for 0.5 h, the reaction mixture was poured into 100 ml of saturated $NaHCO_3$. The organic portion was dried over $MgSO_4$, filtered and transferred to a dry 300 ml flask (total volume ≈110 ml). The flask was cooled to −78 °C, and to it was added all of the solution (prepared in Part A) dropwise. This mixture was stirred at −78 °C for 10 min before warming to room temp. with continued stirring for 1 h. The reaction mixture was poured into 100 ml of saturated $NaHCO_3$ and washed with H_2O (3 × 100 ml). The organic layer was dried over $MgSO_4$, after removing solvents, 8.7 g crude material was obtained, and was about 85% pure by GC analysis, which was identified as **16** by ^{19}F NMR analysis, δ_F −145.12 (t of d, *J* 128, 23, 1F), −173.96 (d, *J* 126, 1F).

Part C: 1,2-difluoro-6-bromohex-1-ene (1e). To a 250 ml flask were added 100 ml of DMF, 5 ml of H_2O and 10 g of KF, and the mixture was stirred until the solids were dissolved in the solution. All of the crude material obtained in Part B was added to the flask and stirred at room temp. for 12 h, after which 150 ml of diethyl ether was added to the flask and the solution washed with brine (3 × 100 ml), and then with H_2O (2 × 50 ml). The organic portion was dried over $MgSO_4$, and solvents were removed by rotary evaporator. The residue was placed in a 250 ml flask, and to it was added 50 ml (2 × 0.024 mol) of Bu_4NF (Aldrich, 1.0 M in THF) in 100 ml of dry THF, and the mixture stirred at room temp. for 24 h. The THF was removed by rotary evaporator, and the reaction mixture was worked up in the usual manner (as described in Part B). The mixture was purified by distillation under reduced pressure. ^1H and ^{19}F NMR analysis of the distillate indicated that it was 5,6-difluorohex-5-enol (**17**), δ_H 1.61 (m, 4H), 2.41 (m, 2H), 2.62 (br, 1H), 3.61 (t, *J* 7, 2H), 7.08 (d of d, *J* 117, 1H); δ_F −160.73 (t of d, *J* 192, 34, 1F), −183.78 (d of d, *J* 192, 116, 1F).

As described in the synthesis of **1b**, 5,6-difluorohex-5-enol was converted to 1,2-difluoro-6-bromohex-1-ene (**1e**). The final purification was by column chromatography to give 2.1 g. The overall yield (based on the trimethylsilyl iodide) was 21%, δ_H 1.73 (m, 2H), 1.92 (m, 2H), 2.42 (m, 2H), 3.43 (t, *J* 7, 2H), 7.09 (d of d, *J* 75, 3, 1H); δ_C 23.8, 24.9, 25.2, 31.6, 33.0, 138.1 (d), 141.3 (d); δ_F −160.37 (t of d, *J* 128, 23, 1F), −182.81 (d of d, *J* 128, 76, 1F); (Calc. for $C_6H_9F_2Br$: 197.9856. Found: 197.9821).

1,2-Difluorohex-1-ene (3e) and 1-fluoromethyl-1-fluorocyclopentane (5e)

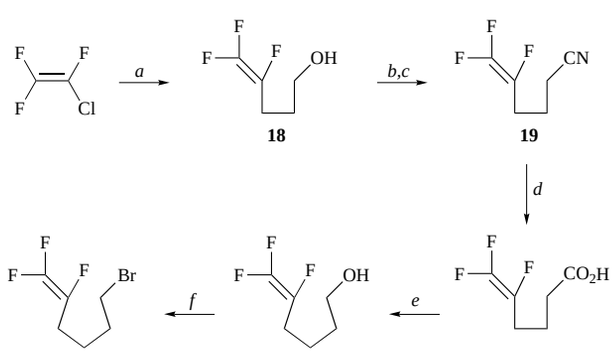
Preparation of **3e** and **5e** was carried out by the same procedures as those used for the preparation of **3b** and **5b**.

1,2-Difluorohex-1-ene (3e). δ_H 0.94 (t, *J* 7, 3H), 1.39 (m, 2H), 1.54 (m, 2H), 2.39 (m, 2H), 7.07 (d of d, *J* 77, 3, 1H); δ_F −160.12 (t of d, *J* 130, 23, 1F), −183.79 (d of d, *J* 128, 77, 1F); (Calc. for $C_6H_{10}F_2$: 120.0751. Found: 120.0747).

1-Fluoromethyl-1-fluorocyclopentane (5e). δ_H 1.18–1.34 (m, 4H), 1.57 (m, 4H), 4.03 (d of d, *J* 48, 20, 2H); δ_F −150.44 (br, 1F), −224.51 (d of t, *J* 48, 14, 1F); (Calc. for $C_6H_{10}F_2$: 120.0751. Found: 120.0751).

Synthesis of 1,1,2-trifluoro-6-bromohex-1-ene (1f)

The first step in the synthesis of 1,1,2-trifluoro-6-bromohex-1-ene was the key step adapted from a procedure described by Sauvetre.[58] The complete six step synthesis is described as follows (Scheme 8).



Scheme 8 *Reagents and conditions:* (*a*) Bu^tLi, trimethylene oxide–BF_3, Et_2O, −110 °C; (*b*) TsCl–pyridine, 0 °C; (*c*) KCN, DMSO, 0 °C; (*d*) H_2O–HCl, reflux; (*e*) $LiAlH_4$; (*f*) TsCl–pyridine, then LiBr–DMF

4,5,5-Trifluoropent-4-enol (18). 300 ml of dry diethyl ether was placed in a dry 1000 ml round-bottom flask and cooled to −100 °C (liquid nitrogen + diethyl ether). Under argon, 53 g (0.455 mol) of chlorotrifluoroethylene was transferred to the flask. Then, 270 ml (0.459 mol) of Bu^{t}Li (1.7 M in pentane, Aldrich) was added to the solution dropwise through an additional funnel. After addition of Bu^{t}Li, the mixture was stirred for 0.5 h at −110 °C, and then 60 g (0.455 mol) of BF_3 etherate (Aldrich) was added by syringe into the solution. 8.8 g (0.152 mol) of trimethylene oxide (Aldrich) was added to the solution slowly in order to keep the temperature at −110 °C. After addition of trimethylene oxide, the mixture was stirred for 10 min, and then the temperature was allowed to rise to −78 °C and stirred for 1 h. 250 ml of saturated $NaHCO_3$ was poured into the reaction mixture and the temperature raised to room temp. The organic portion was washed with brine (2 × 200 ml) and dried over $MgSO_4$. After distillation,16.2 g of alcohol **18** was obtained (76% yield), δ_H 1.75 (m, 2H), 2.34 (m, 2H), 3.14 (br, 1H), 3.61 (t, *J* 7, 2H); δ_F −106.03 (d of d, *J* 89, 32, 1F), −125.11 (d of d, *J* 116, 89, 1F), 174.76 (m, 1F).

4,5,5-Trifluoropent-4-enylnitrile (19). To a 500 ml dry, round-bottom flask was added 16.0 g (0.114 mol) of **18** with 200 ml of dry pyridine. The mixture was cooled to 0 °C, and then 35 g (0.18 mol) of tosyl chloride was added and the mixture was stirred for 6 h. The mixture was poured into 50 ml of H_2O and extracted with methylene chloride (3 × 100 ml). Distillation of the organic phase gave a light yellow oil (tosylated alcohol) that was used directly in the next step. 30 g (0.45 mol) of potassium cyanide in 500 ml DMSO was placed in a 1000 ml round-bottom flask and cooled to 0 °C. The tosylated alcohol (approx. 0.114 mol) was syringed into the flask, and the mixture was stirred for 20 min before removing the ice bath. The temperature was allowed to rise to room temp., and then the mixture was stirred for 1.5–2 h (not more than 2.5 h). 100 ml of H_2O was poured into the flask and the organic portion was extracted with diethyl ether (4 × 200 ml). All of the diethyl ether solutions were combined and washed with brine (4 × 100 ml), and distillation of the resultant solution gave 13.6 g (81% yield based on the alcohol) of **19**, δ_H 1.87 (m, 2H), 2.39 (m, 4H); δ_F −103.91 (d of d, *J* 85, 32, 1F), −123.38 (d of d, *J* 114, 85, 1F), −175.29 (m, 1F).

5,6,6-Trifluorohex-5-enol (21). In a 300 ml flask attached to a reflux condenser was placed a mixture of 13.5 g (0.091 mol) of **19** and 50 ml of concentrated hydrogen chloride. The mixture was heated to reflux (became dark), and then stirred for 4–5 h under reflux. 150 ml of H_2O was added, the solution was extracted with diethyl ether (4 × 100 ml), and distillation of the resultant solution gave 8.5 g (55% yield) of carboxylic acid **20**, δ_H 1.89 (m, 2H), 2.39 (m, 4H), 4.78 (b, 1H); δ_F −104.88 (m, 1F), −124.31 (m, 1F), −176.67 (m, 1F). To 55 ml of a solution of lithium aluminum hydride (1.0 M in diethyl ether) in a 250 ml round-bottom flask was added 8.5 g (0.051 mol) of **20**. The mixture was stirred at room temp. for 5 h. 10 ml of water was added to the flask, and the mixture was extracted with diethyl ether (3 × 50 ml), and distillation gave **21** (6.5 g, 85% yield), δ_H 1.63–1.65 (m, 4H), 2.32 (m, 2H), 2.56 (br, 1H), 3.66 (t, *J* 7, 2H); δ_F −106.77 (d of d, *J* 90, 32, 1F), −125.82 (d of d, *J* 114, 90, 1F), −175.25 (m, 1F).

Through tosylation and bromination (see the procedure in the synthesis of **1b**), **21** was converted to 1,1,2-trifluoro-6-bromohex-1-ene (**1f**). Purification was by column chromatography to give 4.8 g (overall yield based on the trimethylene oxide: 15%).

1,1,2-Trifluoro-6-bromohex-1-ene (1f). δ_H 1.74 (m, 2H), 1.93 (m, 2H), 2.33 (m, 2H), 3.44 (t, *J* 7, 2H); δ_F −105.21 (d of d, *J* 88, 32, 1F), −124.54 (d of d, *J* 114, 89, 1F), −174.53 (m, 1F); (Calc. for $C_6H_8F_3Br$: 215.9762. Found: 215.9772).

1,1,2-Trifluorohex-1-ene (3f) and 1-difluoromethyl-1-fluorocyclopentane (5f)

Preparation of **3f** and **5f** was accomplished by the same procedures as those used in the preparation of **3c** and **5c**.

1,1,2-Trifluorohex-1-ene (3f). δ_H 0.94 (t, *J* 7, 2H), 1.37 (m, 2H), 1.52 (m, 2H), 2.28 (m, 2H); δ_F −106.74 (d of d, *J* 90, 32, 1F), −125.84 (d of d, *J* 114, 90, 1F), −174.84 (m, 1F); (Calc. for $C_6H_9F_3$: 138.0656. Found: 138.0625).

1-Difluoromethyl-1-fluorocyclopentane (5f). δ_H 1.40–1.75 (m, 2H), 1.85–1.96 (m, 4H), 1.97–2.05 (m, 2H), 5.84 (d of t, *J* 57, 5, 1H); δ_F −131.50 (d of d, *J* 56, 8, 2F), −158.30 (br, 1F), −174.53 (m, 1F); (Calc. for $C_6H_9F_3$: 138.0656. Found: 138.0664).

1,1,2,3,3,4,4-Heptafluoro-6-bromohex-1-ene (1g)

The title compound was prepared[59] from 1,1,2,3,3,4,4-heptafluoro-6-chlorohex-1-ene which was provided by DuPont Central Research and Development. A mixture of this chloride (2.45 g, 0.0123 mol), 25 ml CH_2Br_2 and 2.16 g (0.0246 mol) LiBr in 50 ml DMF was heated and stirred at 100 °C for 6 h. GC analysis indicated the reaction finished and a distillation (20 mmHg, room temp.) of the reaction mixture gave a mixture of CH_2Br_2 and **1g**. Further separation by preparative GC yielded 1.75 g of the title compound, **1g** (60% yield), δ_H 2.69 (m, 2H), 3.52 (t, *J* 8, 2H); δ_F −89.48 (m, 1F), −106.74 (m, 1F), −115.72 (t, *J* 17, 2F), −119.39 (m, 2F), −187.89 (m of d, *J* 117, 1F); (Calc. for $C_6H_4F_7Br$: 287.9385. Found: 287.9374).

1,1,2,3,3,4,4-Heptafluorohex-1-ene (3g) and 1-difluoromethyl-1,2,2,3,3-pentafluorocyclopentane (5g)

The title compounds were prepared from the bromide **1g** following the same procedure as that used in preparation of **3m** and **5m** from **1m**.

1,1,2,3,3,4,4-Heptafluorohex-1-ene (3g). δ_H 1.12 (t, *J* 7, 3H), 2.06 (m, 2H); δ_F −91.17 (m, 1F), −107.74 (m, 1F), −118.35 (t, *J* 18, 2F), −119.97 (m, 2F), −188.13 (m of d, *J* 116, 1F); (Calc. for $C_6H_5F_7$: 210.0279. Found: 210.0280).

1-Difluoromethyl-1,2,2,3,3-pentafluorocyclopentane (5g). δ_H 2.27–2.5 (br, 4H), 5.97 (d of t, *J* 53, 7, 1H); δ_F −111.47 (m of d, *J* 244, 1F), −118.98 (d, *J* 246, 1F), −130.03 (d, *J* 259, 1F), −132.89 (d, *J* 259, 1F), −133.68 (t of d, *J* 53, 7, 1F), −133.98 (t of d, *J* 53, 10, 1F), −182.24 (s, 1F); (Calc. for $C_6H_5F_7$: 210.0279. Found: 210.0262).

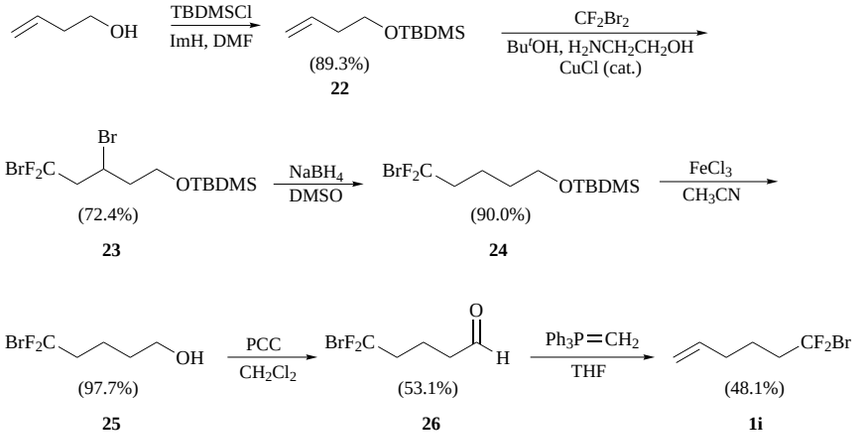
6-Bromoperfluorohex-1-ene (2h)

The title compound was supplied by DuPont Central Research and Development. Further treatment with sodium hydride was needed to remove impurities of acids from the sample, δ_F −63.91 (s, 2F), −88.77 (m, 1F), −105.45 (m, 1F), −177.89 (s, 2F), −118.53 (s, 2F), −123.89 (s, 2F), −189.04 (m, 1F); (Calc. for $C_6F_{11}Br$: 359.9008. Found: 359.9042).

1,1,2,3,3,4,4,5,5,6,6-Undecafluorohex-1-ene (3h) and difluoromethylperfluorocyclopentane (5h)

Under ambient light, the bromide **1h** reacted quickly and quantitatively with tributyltin hydride to give reduced product **3h** (as major product) and cyclized product, difluoromethylperfluorocyclopentane (**5h**). To a mixture of 20 ml of benzene and 0.98 g (3.33 mmol) of Bu_3SnH in a 25 ml flask was added 1.0 g (2.78 mmol) of bromide **1h** and the mixture was stirred for 30 min. The tin compounds were removed by careful distillation of the reaction mixture (*ca.* 55 °C for the oil bath and the receiver for the distillate being cooled to 0 °C). Further purification was by preparative GC. Because of the close boiling points of compounds **3h** and **5h**, the separation of the two compounds was not good enough to isolate them efficiently. Fortunately, the reduction of **1h** by tin hydrides is much faster than its intramolecular cyclization, and the sample obtained in this manner after preparative GC was >91% pure.

1,1,2,3,3,4,4,5,5,6,6-Undecafluorohex-1-ene (3h). δ_H 5.05 (t of t, *J* 51, 5, 1H); δ_F −87.82 (m, 1F), −105.08 (m, 1F), −118.53 (s,



Scheme 9

2F), −125.47 (s, 2F), −129.77 (s, 2F), −136.97 (d, *J* 50, 2F), −188.66 (m, 1F); (Calc. for $C_6H_1F_{11}$: 281.9903. Found: 281.9899).

(Difluoromethyl)perfluorocyclopentane (5h). δ_H 5.26 (d of t, *J* 50, 12, 1H); δ_F −124.17 (d, *J* 285, 2F), −128.43 (d, *J* 265, 2F), −130.55 (d, *J* 290, 2F), −131.97 (d, *J* 273, 2F), −135.48 (d, *J* 54, 2F), −200.18 (s, 1F); (Calc. for $C_6H_1F_{11}$: 281.9903. Found: 281.9917).

Synthesis of 6-bromo-6,6-difluorohex-1-ene (1i)

1-(*tert*-Butyldimethylsiloxyl)but-3-ene (22). Into a 250 ml three-necked round-bottomed flask equipped with a condenser and argon inlet was placed 9.60 g (1.33×10^{-1} mol) of but-3-en-1-ol, 20 ml DMF, 24.1 g (1.60×10^{-1} mol) *tert*-butyldimethylsilyl chloride, and 22.7 g (3.33×10^{-1} mol) imidazole (Scheme 9). This was stirred for 48 h at room temperature under an argon atmosphere. The contents of the flask were then poured into 250 ml of pentane, and washed with three 50 ml portions of water followed by three 50 ml portions of saturated aqueous sodium chloride. The organic phase was dried, the solvent rotary evaporated, and the resulting liquid subjected to fractional reduced pressure distillation through a 15 cm Vigreux column. A total of 22.08 g (89.3%) of pure **22** was obtained in four fractions as a colorless liquid, bp 102–105 °C/75 mmHg, δ_H 0.05 (6H, s), 0.90 (9H, s), 2.27 (2H, dt, $^3J_{HH}$ 7, $^3J_{HH}$ 3), 3.66 (2H, t, $^3J_{HH}$ 7), 5.02 (1H, m), 5.10 (1H, m), 5.81 (1H, m); δ_C −5.27, 18.3, 25.9, 37.5, 62.8, 116.2, 135.4; [Calc. for $C_{10}H_{22}SiO$: 186.1440. Found (M + H): 187.1561. For $C_{10}H_{22}SiO$: Calc. C, 64.45; H, 11.90. Found: C, 64.32; H, 12.03%].

1,3-Dibromo-5-(*tert*-butyldimethylsiloxyl)-1,1-difluoropentane (23). (0.10 g, 1.25×10^{-3} mol) cuprous chloride, 12.5 ml Bu^tOH, 3.83 g (6.26×10^{-2} mol) ethanolamine, 23.30 g (1.25×10^{-1} mol) **22**, and 52.60 g (2.51×10^{-1} mol) CF_2Br_2 were added to a Carius tube. A small stir bar was added and the tube flame-sealed. After stirring at 85 °C for 96 h (performed behind a safety shield) the tube was cooled in an ice bath, opened, and the contents transferred to a 500 ml Erlenmeyer flask. The tube was rinsed with four 50 ml portions of hexanes, and the combined organic material filtered through a 50 ml pad of silica gel, which was rinsed with three additional 50 ml portions of hexanes. Rotary evaporation of the solvent afforded a colorless liquid judged by ^1H NMR spectroscopy to contain some unreacted starting material, 2.78 g of which was successfully recovered by reduced pressure distillation at 102–105 °C/75 mmHg. High vacuum was then applied and a total of 35.83 g (72.4%, 82.0% based on consumed **22**) of **23** was obtained as a colorless liquid, bp 75–79 °C/0.09 mmHg, δ_H 0.07 (3H, s), 0.08 (3H, s), 0.90 (9H, s), 1.95 (1H, m), 2.15 (1H, m), 3.08 (2H, m), 3.80 (2H, m), 4.46 (1H, m); δ_C −5.5, 18.2, 25.9, 41.3, 43.8, 52.9 (t, $^2J_{CF}$ 19), 60.2, 120.64 (t, $^1J_{CF}$ 306); δ_F −43.1 (m); [Calc. for $C_{11}H_{22}SiOF_2Br_2$: 393.9774; Calc. (M − *t* − C_4H_9): 336.9070. Found: 336.905. For $C_{11}H_{22}SiOF_2Br_2$: Calc. C, 33.35; H, 5.60. Found: C, 33.62; H, 5.62%].

1-Bromo-5-(*tert*-butyldimethylsiloxyl)-1,1-difluoropentane (24). 30.15 g (7.60×10^{-2} mol) **23** was dissolved in 150 ml of dry DMSO in a 500 ml three-necked round-bottomed flask equipped with an argon inlet and strong magnetic stir bar. 11.5 g (3.04×10^{-1} mol) of sodium borohydride was then added in portions with vigorous stirring. After the addition was complete, the temperature was raised to 70–75 °C over the course of 1 h and stirring continued for an additional 6 h, at which time analysis of the reaction mixture by ^{19}F NMR spectroscopy demonstrated complete consumption of starting material. The flask was cooled and carefully quenched with *ca.* 100 g of ice, and the contents carefully acidified with concentrated hydrochloric acid and transferred to a 1 l separatory funnel. After extraction with three 100 ml portions of diethyl ether, the combined extracts were washed with two 25 ml portions of water, dried over $MgSO_4$, and rotary evaporated. The remaining liquid was distilled at reduced pressure through a 15 cm Vigreux column, affording 21.70 g (90.0%) **24** as a colorless liquid, bp 108–111 °C/10 mmHg, δ_H 0.05 (6H, s), 0.90 (9H, s), 1.63 (4H, m), 2.38 (2H, m), 3.63 (2H, t, $^3J_{HH}$ 6); δ_C 18.3, 20.7, 25.9 (2C, overlapping), 31.4, 44.1 (t, $^2J_{CF}$ 22.5), 62.4, 123.2 (t, $^1J_{CF}$ 304); δ_F −44.0 (m); [Calc. for $C_{11}H_{23}SiOF_2Br$: 316.0669. Found (M + H): 317.0630].

5-Bromo-5,5-difluoropentan-1-ol (25). Into a 250 ml round-bottomed flask was placed 15.04 g (4.74×10^{-2} mol) **24** along with 14 ml of acetonitrile. To this was slowly added with stirring 7.70 g (4.75×10^{-2} mol) of PCC. The reaction mixture turned a brick-red color and became slightly warm. The reaction was allowed to stir for 3 h at room temp., at which time the contents of the flask were poured into 250 ml of water and 100 ml of chloroform was added. The chloroform layer was drained and the aqueous layer extracted with three 50 ml portions of chloroform. These combined extracts were washed twice with 25 ml of water, dried over $MgSO_4$ and the solvent rotary evaporated. 9.41 g (97.7%) **25** was collected by fractional reduced pressure distillation, bp 80–82 °C/10 mmHg, δ_H 1.39 (1H, s), 1.69 (4H, m), 2.40 (2H, m), 3.69 (2H, t, $^3J_{HH}$ 6); δ_C 20.5, 31.3, 44.0 (t, $^2J_{CF}$ 21.5), 62.2, 123.0 (t, $^1J_{CF}$ 303.5); δ_F −44.1 (t, $^3J_{FH}$ 14.7); [Calc. for $C_5H_9F_2BrO$: 201.9804. Found (M + H): 202.9957. For $C_5H_9F_2BrO$: Calc. C, 29.58; H, 4.47. Found: C, 29.71; H, 4.46%].

5-Bromo-5,5-difluoropentanal (26). Into a 250 ml flask equipped with a magnetic stir bar was added 8.5 g (4.18×10^{-2} mol) **25** dissolved in 85 ml of dichloromethane. 13.53 g (6.28×10^{-2} mol) of PCC was added slowly in portions with vigorous stirring. After the addition was complete, the mixture was allowed to stir at room temp. for an additional 6 h. The darkened reaction mixture (which demonstrated complete consumption of starting material by TLC analysis) was filtered through a pad of silica gel, which was rinsed with an additional

three 10 ml portions of CH_2Cl_2. Rotary evaporation of the solvent followed by fractional distillation at reduced pressure afforded 4.46 g (53.1%) **26** as a colorless liquid, bp 100–102 °C/50 mmHg, δ_H 1.97 (2H, m), 2.41 (2H, m), 2.59 (2H, t, $^3J_{HH}$ 7.2), 9.80 (1H, s); δ_C 16.6 (t, $^3J_{CF}$ 3.5), 42.1, 43.2 (t, $^2J_{CF}$ 22.0), 122.5 (t, $^1J_{CF}$ 303.4), 200.5; δ_F −44.4 (t, $^3J_{FH}$ 14.4); [Calc. for $C_5H_7F_2$-BrO: 199.9648. Found (M + H): 200.9726].

6-Bromo-6,6-difluorohex-1-ene (1i). A 100 ml three-necked round-bottomed flask equipped with self-equalizing additional funnel, argon inlet and magnetic stir bar was charged with 9.12 g (2.55×10^{-2} mol) of methyltriphenylphosphonium bromide and 20 ml anhydrous THF. The flask was cooled to 0 °C and 9.4 ml of a 2.5 M solution of butyllithium in hexanes (2.35×10^{-2} mol) was added dropwise. After addition was complete, the mixture was stirred for an additional 30 min at 0 °C. 4.28 g (2.13×10^{-2} mol) **26** was dissolved in 20 ml anhydrous THF and added dropwise to the reaction mixture. After addition the mixture was allowed to warm to room temp. and stirred for an additional 6 h. The contents were poured into 50 ml of water and extracted with five 20 ml portions of diethyl ether. The combined diethyl ether fractions were dried over $MgSO_4$, filtered, and the solution concentrated by distillation through a 15 cm Vigreux column. Upon removal of most of the diethyl ether and residual THF the product was distilled at ambient pressure, yielding 2.04 g (48.1%) **1i**, bp 120–123 °C. An analytically pure sample was obtained by preparative GC for spectroscopic analysis and kinetic experiments, δ_H 1.74 (2H, m), 2.15 (2H, overlapping dt, $J = 7$), 2.35 (2H, m), 5.05 (2H, m), 5.77 (1H, m); δ_C 23.1, 32.3, 43.6 (t, $^2J_{CF}$ 21.6), 115.9, 123.1 (t, $^1J_{CF}$ 303.5), 137.0; δ_F −43.9 (t, $^3J_{FH}$ 14.7); [Calc. for $C_6H_9F_2Br$: 197.9855; Calc. (M − Br): 119.0672. Found: 119.0667. For $C_5H_9F_2Br$: Calc. C, 36.21; H, 4.56. Found: C, 36.28; H, 4.56%].

5,5-Difluorohex-1-ene (3i)

1.0 g (5.02×10^{-3} mol) **1i** was treated with 1.6 g (5.50×10^{-3} mol) of tributyltin hydride in a manner identical to the independent preparation of **3j**. Flash distillation followed by preparative GC separation afforded pure **3i**, δ_H 1.60 (3H, t, $^3J_{HF}$ 18), 1.94 (2H, m), 2.24 (2H, m), 5.03 (2H, m), 5.83 (1H, m); δ_C 23.3 (t, $^2J_{CF}$ 28.1), 26.9 (t, $^3J_{CF}$ 5.0), 37.2 (t, $^2J_{CF}$ 25.1), 115.2, 123.9 (t, $^1J_{CF}$ 236.4), 136.9; δ_F −91.3 (m); (Calc. for $C_6H_{10}F_2$: 120.0751. Found: 120.0743).

1,1-Difluoro-3-methylcyclopentane (5i)

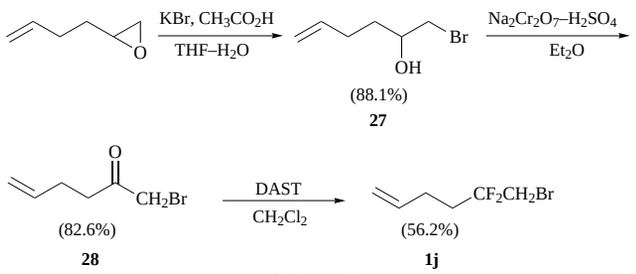
0.5 g (5.09×10^{-3} mol) of 3-methylcyclopentanone and 0.9 g (5.58×10^{-3} mol) diethylaminosulfur trifluoride (DAST) were reacted in 10 ml of anhydrous CH_2Cl_2 in a manner identical to the preparation of **5j**. Flash distillation and preparative GC separation afforded pure **5i**, δ_H 1.05 (3H, d, $^3J_{HH}$ 6), 1.36 (1H, m), 1.61 (1H, m), 1.87–2.31 (5H, m); δ_C 20.0, 31.6, 32.0 (t, $^3J_{CF}$ 4.3), 36.0 (t, $^2J_{CF}$ 25.0), 44.0 (t, $^2J_{CF}$ 23.6), 133.0 (t, $^1J_{CF}$ 246.9); δ_F −88.9 (1F, dm, $^2J_{FF}$ 217.1), −90.2 (1F, dm, $^2J_{FF}$ 227.1); (Calc. for $C_6H_{10}F_2$: 120.0751. Found: 120.0759).

1,1-Difluorocyclohexane (6i)

0.5 g (5.09×10^{-3} mol) of cyclohexanone and 0.9 g (5.58×10^{-3} mol) DAST were reacted in 10 ml of anhydrous CH_2Cl_2 in a manner identical to the preparation of **5j**. Flash distillation and preparative GC separation afforded pure **6i**, δ_H 0.97 (2H, m), 1.29 (4H, q, $^3J_{HH}$ 6), 1.58 (4H, m); δ_C 22.8, 24.4, 34.1 (t, $^2J_{CF}$ 23.5), 123.6 (t, $^1J_{CF}$ 239.9); δ_F −95.7 (2F, br s).

Synthesis of 6-bromo-5,5-difluorohex-1-ene (1j)

6-Bromohex-1-en-5-ol (27). In accordance with a procedure by Cory and Su,[60] to a 500 ml three-necked round-bottomed flask equipped with magnetic stirrer was added 100 ml acetic acid, 50 ml of saturated aqueous potassium bromide, and 50 ml THF (Scheme 10). The flask was cooled to 0 °C and 5.0 g (5.09×10^{-2} mol) of 1,2-epoxyhex-5-ene dissolved in 10 ml of



Scheme 10

THF was added dropwise with stirring. The heterogeneous mixture was stirred at 0 °C for an additional 2 h, then allowed to warm to room temp. and stirred overnight. Most of the THF was removed by rotary evaporation, 100 ml of diethyl ether and 50 ml of water was added, and the aqueous layer washed with saturated aqueous $NaHCO_3$ until the acetic acid was removed. Drying over $MgSO_4$ followed by rotary evaporation of the solvent afforded 8.03 g (88.1%) **27** which was used in the next step without further purification, δ_H 1.61 (2H, overlapping dt, J 8), 2.15 (2H, m), 2.67 (1H, s), 3.35 (1H, m), 3.48 (1H, m), 3.76 (1H, m), 4.99 (2H, m), 5.77 (1H, m); δ_C 29.6, 34.0, 40.0, 70.2, 115.2, 137.5; [Calc. for $C_6H_{11}BrO$: 177.9993. Calc. (M + H): 178.9993. Found: 179.0058].

1-Bromohex-5-en-2-one (28). 7.25 g (4.05×10^{-2} mol) **27** dissolved in 10 ml diethyl ether was added dropwise to a mixture of 60 ml of Jones' reagent and 25 ml diethyl ether at room temp. with stirring. After 4 h the dark green reaction mixture was diluted with 50 ml of water. The layers were separated and the aqueous layer extracted with three 20 ml portions of diethyl ether. The combined organic extracts were washed twice with 20 ml of saturated aqueous $NaHCO_3$ and once with 20 ml of water. Drying and rotary evaporation of the solvent afforded 5.92 g (82.6%) **28** which was used without further purification, δ_H 2.35 (2H, overlapping dt, J 6), 2.74 (2H, t, $^3J_{HH}$ 7), 3.88 (2H, s), 5.01 (2H, m), 5.78 (1H, m); δ_C 27.7, 34.2, 38.8, 115.7, 136.3, 201.2; (Calc. for C_6H_9BrO: 175.9836. Found: 175.9850).

6-Bromo-5,5-difluorohex-1-ene (1j). A 100 ml three-necked round-bottomed flask equipped with an argon inlet, rubber septum and magnetic stirrer was charged with 2.1 g (1.19×10^{-2} mol) **28** in 20 ml of anhydrous CH_2Cl_2. The flask was cooled to 0 °C and 1.9 ml (2.32 g, 1.44×10^{-2} mol) of DAST was slowly injected into the reaction mixture with stirring. After 2 h at 0 °C, the flask was allowed to warm to room temp. and stirring continued for an additional 48 h. The contents were carefully dispensed onto 20 g of ice, the layers separated, and the aqueous layer extracted twice with 5 ml CH_2Cl_2. The combined organic extracts were washed once with 10 ml of saturated aqueous $NaHCO_3$ and once with 10 ml of water. After drying over $MgSO_4$ the solution was carefully concentrated *via* gentle ambient pressure distillation. 1.33 g (56.2%) **1j** was obtained as a colorless liquid, bp 117–119 °C, which was further purified by preparative GC for spectroscopic analysis and kinetic experiments, δ_H 2.06–2.31 (4H, m), 3.53 (2H, t, $^3J_{HF}$ 13), 5.07 (2H, m), 5.82 (1H, m); δ_C 26.2 (t, $^3J_{CF}$ 4.5), 31.3 (t, $^2J_{CF}$ 33.6), 33.8 (t, $^2J_{CF}$ 24.1), 115.8, 121.1 (t, $^1J_{CF}$ 241.4), 136.2; δ_F −99.3 (m); (Calc. for $C_6H_9F_2Br$: 197.9855. Found: 197.9850. For $C_6H_9F_2Br$: Calc. C, 36.21; H, 4.56. Found: C, 36.16; H, 4.57%).

6,6-Difluorohex-1-ene (3j)

1.0 g (5.02×10^{-3} mol) **1j** was dissolved in 1 ml of mesitylene in a 10 ml round-bottomed flask equipped with a septum-capped side arm inlet and small stir bar. This was attached to an ice–water-cooled micro distillation apparatus. 1.6 g (5.50×10^{-3} mol) of tributyltin hydride was slowly injected into the flask through the septum. When the addition was complete, the flask was heated on an oil bath. After 15 min at 50 °C, the temperature was quickly raised and all volatile material was flash distilled into an ice-cooled receiver until the bath temperature

reached 150 °C. The distillate was subjected to preparative GC separation affording pure **3j**, δ_H 1.57 (2H, m), 1.83 (2H, m), 2.12 (2H, overlapping dt, *J* 7), 5.00 (2H, m), 5.79 (1H, m), 5.81 (1H, tt, $^3J_{HH}$ 4, $^2J_{HF}$ 57); δ_C 21.3, 32.9, 33.8 (t, $^2J_{CF}$ 20.5), 115.4, 117.3 (t, $^1J_{CF}$ 237.6), 120.5; δ_F −116.4 (dt, $^3J_{FH}$ 14.6, $^2J_{FH}$ 59.8); (Calc. for $C_6H_{10}F_2$: 120.0751. Found: 120.0756. For $C_6H_{10}F_2$: Calc. C, 59.98; H, 8.39. Found: C, 59.96; H, 8.47%).

1,1-Difluoro-2-methylcyclopentane (5j)

Into a 50 ml three-necked round-bottomed flask equipped with magnetic stirrer and septum was placed 0.5 g (5.09×10^{-3} mol) 2-methylcyclopentanone dissolved in 10 ml of anhydrous CH_2Cl_2. 0.9 g (5.58×10^{-3} mol) DAST was then injected and the mixture stirred at room temp. overnight. The reaction was dispensed onto *ca.* 2 g of ice, the layers separated, and the organic layer washed with 1 ml of saturated aqueous $NaHCO_3$. After drying, all volatile material was flash distilled and subjected to preparative GC, affording pure **5j**, δ_H 1.04 (3H, d, $^3J_{HH}$ 7), 1.40 (1H, m), 1.73 (2H, m), 2.04 (4H, overlapping m); δ_C 12.1, 19.9, 30.9, 34.4 (t, $^2J_{CF}$ 25.1), 40.7 (t, $^2J_{CF}$ 23.5), 132.4 (t, $^1J_{CF}$ 249.4); δ_F −100.2 (1F, d of overlapping dt, $^3J_{FH}$ 12.2, $^2J_{FF}$ 225.8), −107.6 (1F, d of overlapping dt, $^3J_{FH}$ 17.1, $^2J_{FF}$ 224.6); (Calc. for $C_6H_{10}F_2$: 120.0751. Found: 120.0748).

The syntheses and characterizations of 1-bromo-1,1,2,2-tetrafluorohexane, 1,1,2,2-tetrafluorohexane and 3,3,4,4-tetrafluoro-1-phenyloctane have been reported elsewhere.[17]

5,5,6,6-Tetrafluorohex-1-ene (3k), 1,1,2,2-tetrafluoro-3-methylcyclopentane (5k) and 1,1,2,2-tetrafluorocyclohexane (6k)

5.0 g (2.13×10^{-2} mol) of 6-bromo-5,5,6,6-tetrafluoro-1-ene (**1k**) (obtained as a gift from Halocarbons, Inc.) dissolved in 5 ml of mesitylene was added to a 50 ml three-necked flask equipped with ice–water condenser, argon inlet, magnetic stir bar and rubber septum. 7.5 g (2.58×10^{-2} mol) of tributyltin hydride and 0.05 g (3.04×10^{-4} mol) 2,2′-azoisobutyronitrile (AIBN) in 5 ml of mesitylene was taken up into a syringe. The flask was heated at 50 °C and irradiated with a 150 W flood lamp placed at a distance of *ca.* 1 m while the Bu^n_3SnH solution was delivered to the reaction mixture, *via* syringe pump, over a 24 h period. After the addition was complete, volatile material was flash distilled from the reaction mixture until the bath temperature reached 150 °C. Purification by preparative GC afforded pure samples of **3k**, **5k** and **6k**. For **3k**, δ_H 2.06 (2H, m), 2.33 (2H, m), 5.08 (2H, m), 5.72 (1H, tt, $^3J_{HF}$ 3, $^2J_{HF}$ 54), 5.84 (1H, m); δ_C 24.6 (t, $^3J_{CF}$ 4.0), 29.2 (t, $^2J_{CF}$ 22.1), 110.3 (tt, $^2J_{CF}$ 41.1, $^1J_{CF}$ 247.7), 115.9, 117.8 (tt, $^2J_{CF}$ 29.0, $^1J_{CF}$ 244.8), 136.1; δ_F −116.7 (2F, t, $^3J_{FH}$ 17.1), −136.0 (2F, d, $^2J_{FH}$ 56.2); Calc. for $C_6H_8F_4$: 156.0562. Found: 156.0562). For **5k**, δ_H 1.12 (3H, d, $^3J_{HH}$ 7), 1.47 (1H, m), 2.00 (1H, m), 2.07–2.49 (3H, m); δ_C 11.4, 23.7 (m), 29.8 (t, $^2J_{CF}$ 22.8), 36.2 (t, $^2J_{CF}$ 21.0), 117.6–125.8 (2C, m), δ_F −110.1 (1F, dm, $^2J_{FF}$ 234.4), −120.7 (1F, dm, $^2J_{FF}$ 239.3), −126.0 (1F, dt, $^3J_{FH}$ 12.2, $^2J_{FF}$ 236.8), −132.9 (1F, dm, $^2J_{FF}$ 235.6); (Calc. for $C_6H_8F_4$: 156.0562. Found: 156.0563. For $C_6H_8F_4$: Calc. C, 46.16; H, 5.16. Found: C, 46.17; H, 5.35%). For **6k**, δ_H 1.69 (4H, br s), 2.06 (4H, br s); δ_C 21.0, 31.7 (t, $^2J_{CF}$ 22.1), 117.0 (tt, $^2J_{CF}$ 28.1, $^1J_{CF}$ 250.4); δ_F −119.7 (4F, br s); (Calc. for $C_6H_8F_4$: 156.0562. Found: 156.0571).

Synthesis of 4,4,5,5,6,6-hexafluoro-6-iodohex-1-ene (1l)

1,3-Diiodoperfluoropropane. $I(CF_2)_3I$ was prepared from hexafluoroglutaryl dichloride [$ClCO(CF_2)_3COCl$] by treatment with KI by a reported method.[61] However, there was no detailed procedure in the literature. To a stirred suspension of 36 g KI (0.217 mol, dried at 200 °C for 12 h) in a 600 ml pressure reactor was added 18.1 g (0.065 mol) of hexafluoroglutaryl dichloride (PCR, Inc.). The reactor was sealed and argon was pumped in to increase the pressure to 480 psi. The temperature was increased to 200–250 °C (the pressure was as high as 1000 psi at the temperatures) and the reactor stirred for 8 h. The reactor was cooled to room temp. and then, at 0 °C, the pressure in the reactor was relieved by releasing the argon. 200 ml of H_2O was added to the reaction mixture in the reactor and a total of 300 ml of diethyl ether was used to extract this resultant solution. The separated ethereal solution was combined and washed with 40% of sodium thiosulfate (3 × 100 ml, removing iodine from the solution). The resultant mixture was distilled to give 18 g of the title product (68% yield), δ_F −59.45 (s, 4F), −105.43 (s, 2F).

4,4,5,5,6,6-Hexafluoro-6-iodohex-1-ene (1l). Under photolytic conditions, addition of $I(CF_2)_3I$ to allyl bromide in the presence of bis(tributyltin) takes place. Following the elimination of Bu_3SnBr (it was not clear how the elimination occurred) *in situ*, the title product was obtained. The amount of bis(tributyltin) used in the reaction is critical, it cannot be over 0.5 equiv. relative to the iodide since any excess bis(tributyltin) would catalyze intramolecular cyclization of the addition product obtained. To a 0.9 ml (10.2 mmol) of allyl bromide and 4.12 g (10.02 ml) of 1,3-diiodohexafluoropropane with 50 ml of degassed benzene in a quartz photo-reactor was added 1.23 ml (4.59 mmol) of bis(tributyltin). The mixture was stirred and photolyzed by a medium pressure mercury lamp (ACE glass) for 7 h. ^{19}F NMR analysis indicated that the conversion of the iodide was about 50%, any longer photolyzing the reaction mixture caused an increase of the intramolecular cyclization product. The reaction was stopped by removing the lamp, and the mixture was distilled under reduced pressure to remove the tin compounds. The distillate was purified by preparative GC. δ_H 2.85 (d of t, *J* 18, 7, 2H), 5.30–5.34 (m, 2H), 5.81 (m, 1H); δ_F −57.82 (s, 2F), −111.97 (m, 2F), −114.56 (s, 2F); (Calc. for $C_6H_5F_6I$: 317.9339. Found: 317.9327).

4,4,5,5,6,6-Hexafluorohex-1-ene (3l), 1-methyl-2,2,3,3,4,4-hexafluorocyclopentane (5l) and 1,1,2,2,3,3-hexafluorocyclohexane (6l)

The three compounds were prepared from the reaction of **40** with triethylsilane under the photo-initiation conditions. To 0.8 ml of triethylsilane (5.14 mmol) in a Pyrex NMR tube was added 0.1 ml (0.64 mmol) of **1l**, and then the NMR tube was sealed by a rubber septum, and irradiated in a Rayonet photolyzer for 3 days. ^{19}F NMR analysis indicated that the conversion of the starting material was about 85%. Through preparative GC, the title compounds were isolated.

4,4,5,5,6,6-Hexafluorohex-1-ene 3l. δ_H 2.84 (d of t, *J* 19, 6, 2H), 5.29–5.36 (m, 2H), 5.81 (m, 1H), 6.01 (t of t, *J* 54, 6, 1H); δ_F −114.92 (m, 2F), −131.69 (s, 2F), −137.89 (d, *J* 48, 2F); (Calc. for $C_6H_6F_6$: 192.0374. Found: 192.0370).

1-Methyl-2,2,3,3,4,4-hexafluorocyclopentane (5l). δ_H 1.20 (d, *J* 7, 3H), 1.97 (m, 1H), 2.54 (br, 2 H); δ_F −109.46 (d, *J* 244, 1F), −114.61 (t of d, *J* 244, 18, 1F), −120.97 (d, *J* 243, 1F), −130.45 (d of d, *J* 251, 19, 1F), −131.32 (d, *J* 242, 1F), −135.79 (d, *J* 249, 1F); (Calc. for $C_6H_6F_6$: 192.0374. Found: 192.0368).

1,1,2,2,3,3-Hexafluorocyclohexane (6l). δ_H 1.59 (s, 1H), 1.82 (m, 2H), 2.18 (br, 3H); δ_F −117.53 (s, 4F), −138.50 (br, 2F); (Calc. for $C_6H_6F_6$: 192.0374. Found: 192.0362).

3,3,4,4,5,5,6,6-Octafluoro-6-iodohex-1-ene (1m)

The title compound was reported by DuPont Central Research and Development, δ_H 4.94 (m, 1H), 5.43 (m, 2H); δ_F −59.74 (s, 2F), −112.62 (s, 2F), −113.67 (s, 2F), −122.56 (m, 2F); (Calc. for $C_6H_3F_8I$: 353.9151. Found: 353.9183).

3,3,4,4,5,5,6,6-Octafluorohex-1-ene (3m), methyloctafluorocyclopentane (5m) and 1,1,2,2,3,3,4,4-octafluorocyclohexane (6m)

To 0.55 ml of triethylsilane with 0.3 ml of degassed benzene in a Pyrex NMR tube was added 0.27 ml (1.41 mmol) of **1m**. The mixture was photolyzed in a Rayonet photolyzer for 17 h. ^{19}F NMR analysis indicated that the reaction was finished. Through preparative GC, the title compounds were isolated.

3,3,4,4,5,5,6,6-Octafluorohex-1-ene (3m). δ_H 4.98 (m, 1H), 5.21 (t of t, *J* 52, 6, 1H), 5.44 (m, 2H); δ_F −113.73 (s, 2F), −125.47 (s, 2F), −129.50 (s, 2F), −137.05 (d, *J* 57, 2F); (Calc. for $C_6H_4F_8$: 228.0185. Found: 228.0169).

Methyloctafluorocyclopentane (5m). δ_H 0.64 (d, *J* 7, 3H), 2.04 (br, 1H); δ_F −119.49 (d, *J* 244, 2F), −124.84 (d of d, *J* 252, 19, 2F), −130.76 (d, *J* 250, 2F), −134.05 (d, *J* 250, 2F); (Calc. for $C_6H_4F_8$: 228.0185. Found: 228.0174).

1,1,2,2,3,3,4,4-Octafluorocyclohexane (6m). δ_H 1.29 (br, 4H); δ_F −118.19 (s, 4F), −135.152 (br 4F); (Calc. for $C_6H_4F_8$: 228.0185. Found: 228.0164).

Competition kinetics: unimolecular cyclization (k_c) or addition to styrene (k_{add}) *vs.* hydrogen atom abstraction (k_H). General procedure

Into each of a set of six Pyrex NMR tubes was added a known amount of C_6D_6, varying known amounts of styrene and/or hydrogen atom donor, 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–propan-2-ol 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 followed by warming to room temp. with vigorous shaking. The tubes were then generally subjected to UV photolysis in a Rayonet reactor at 30 (±2) °C until complete consumption of starting material was demonstrated by ^{19}F NMR analysis. Product ratios for varied concentrations of hydrogen atom donor (or ratios of hydrogen atom donor to styrene) allow determination of the ratios k_H/k_c or 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 spectrum.

Cyclopolymerization

6,7-Dichloro-4,4,5,5,6,7,7-heptafluoro-2-iodoheptyl acetate. To a stirred solution of 20 g (0.2 mol) allyl acetate and 2.0 of $Pd(PPh_3)_4$ in 10 ml of hexane was added 56.8 g (0.15 mol) of $CF_2ClCFClCF_2CF_2I$[62] at room temp. After the exothermic reaction subsided, the mixture was stirred overnight to give 53.5 g (74.5%) of $CF_2ClCFClCF_2CF_2CH_2CHICH_2OC(O)CH_3$, bp 89–90 °C/0.3 mm, δ_F −64.0 (m, 2F), −110–112.8 (m, 2F), −116.1 (m, 2F), −130.8 (m, 1F); δ_H 4.44–4.28 (m, 3H), 3.05–2.70 (m, 2H), 2.13 (s, 3H); (Calc. for $C_9H_8F_7Cl_2IO_2$: C, 22.57; H, 1.68; F, 27.77; Cl, 14.80; I, 26.50. Found: C, 23.01; H, 1.85; F, 28.92; Cl, 14.79; I, 26.08%).

1,1,2,3,3,4,4-Heptafluorohepta-1,6-diene (9). To a stirred mixture of 10.5 g zinc dust in 20 ml of DMF was added slowly 0.5 g of 1,2-dibromoethane. After stirring for 10 min, 24 g (0.05 mol) of $CF_2ClCFClCF_2CF_2CH_2CHICH_2OC(O)CH_3$ was slowly added and the resulting mixture was stirred for 2 h. The volatiles (6.8 g) were transferred *in vacuo* to a −78 °C trap and then redistilled to give 6.2 g (56%) of pure **9**, bp 87 °C, δ_F −90.7 (ddt, 1F, *J* 55.3, 38.1, 5.7), −107.4 (ddtt, 1F, *J* 112.7, 55.3, 26.9, 3.4), −115.2 (tm, 2F, *J* 18.5), −119.6 (ddd, 2F, *J* 26.9, 14.5), −188.3 (ddt, 1F, *J* 112.7, 38.1, 14.5); δ_H 5.75–5.90 (m, 1H), 5.70 (m, 2H), 2.82 (m, 2H); ν_{max}/cm^{-1} 1789 (s), 1653 (m), 1368 (s), 1318 (5), 1272 (s), 1108 (s) (Calc. for $C_7H_5F_7$: C, 37.85; H, 2.27. Found: C, 37.62; H, 2.28%).

Homopolymerization of 9. A 25 ml glass ampoule fitted with a Teflon® PTFE stirring bar was charged with 0.3 ml of 5% bis(perfluoropropionyl) peroxide (**3P**) in 1,1,2-trichlorotrifluoroethane (CFC-113) and 0.8 g of **9**. The ampoule was sealed and cooled in a liquid N_2 bath. After being evacuated and purged with N_2 alternately six times, the contents of the sealed ampoule were stirred at 40 °C for 23 h. The white, heterogeneous mixture was filtered, washed with ethyl acetate and dried under vacuum at 100 °C to give 0.36 g of polymer, T_g 113 °C, T_m 260 °C (DSC, second heat), δ_F(235 MHz, melt, 270 °C) −103.5 to −130.6 (m, ~6.3F), −163.5 (s, ~0.5F), −181.0 (br m, ~0.09F), −187.7 (s, ~0.42F); thermogravimetric analysis (TGA) (20 °C min^{-1}): 10% wt. loss at ~445 °C (N_2), ~410 °C (air). The IR spectrum showed no absorption around 1790 and 1650 cm^{-1}. The polymer was insoluble in acetone, ethyl acetate, THF, DMF, hexafluorobenzene or FC-75.

The polymerization was repeated in a 75 ml glass ampoule with 0.8 ml of 5% **3P** in CFC-113 and 6.0 g of **9** in 25 g of CFC-113 solvent at 40 °C for 22 h to give 0.25 g of polymer, T_g 106 °C, T_m 258 °C, TGA (20 °C min^{-1}), 10% wt. loss at ~445 °C (N_2), ~420 °C (air); (Calc. for $C_7H_5F_7$: C, 37.85; H, 2.27. Found: C, 36.82; H, 2.17%). The NMR data were identical to that reported above.

The polymerization in a 50 ml gas ampoule with 90 mg AIBN and 6.0 g of **9** in 10 ml of CFC-113 at 70 °C for 60 h gave 3.5 g of essentially identical polymer: T_g 108 °C; T_m 260 °C.

‡ The tables of raw data (Tables 6–18), which were used to calculate the values of k_{C5}, k_{C6} and k_H, are available as supplementary material (SUPPL. No. 57323, 6 pp.). For details of the Supplementary Publications Scheme see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, available *via* the RSC Web page (http://chemistry.rsc.org/suppdata/perkin2/1998/219/).

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