Cyclizations of 5-Hexenyl, 6-Heptenyl, 7-Octenyl, and 8-Nonenyl Radicals. The Kinetic and Regiochemical Impact of Fluorine and Oxygen Substituents[||]

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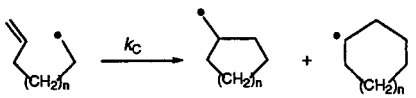
Using competition kinetic methodology, rate constants for cyclizations of a series of hydrofluorocarbon (HFC) and ether 5-hexenyl, 6-heptenyl, and 7-octenyl radicals have been determined. Remarkably large rate constants ($>10^7$ s^{-1}) have been observed for 6-*exo*-cyclizations of 1,1,2,2-tetrafluoro- and 1,1,2,2,3,3,4,4,-octafluoro-6-heptenyl radicals ($>10^3$ those of analogous hydrocarbon radicals), whereas HFC hexenyl and heptenyl ethers exhibit lower cyclization reactivity, as do HFC 7-octenyl radical systems, which cyclize in an *endo* manner. HFC 8-nonenyl radicals were not observed to cyclize. The results can be rationalized in terms of transition state polar influences, though other factors may also play significant roles.

Whereas 5-hexenyl radical cyclizations comprise the ultimate tool for making five-membered rings, use of cyclizations of 6-heptenyl radicals to make six-membered rings is a much less important synthetic technique, with practical cyclizations to form larger rings being almost absent from the literature.[1−3] The reason for this disparity in importance lies, of course, in the large difference in the respective rate constants for such cyclizations (Table 1), the 6-*exo* process being considerably less efficient (50 times slower) than the 5-*exo* process, with cyclization of the 7-octenyl radical being another 45 times slower, its cyclization proceeding exclusively *endo*.[5]

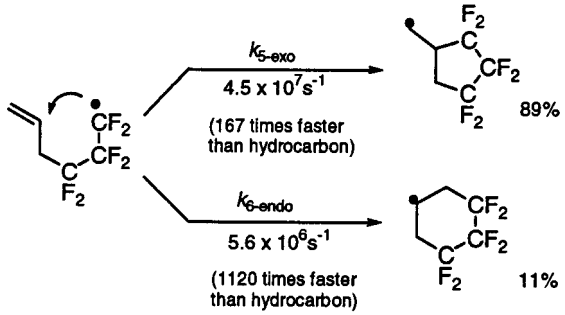
In an earlier comprehensive study, we demonstrated that fluorine substitution at the radical center has a remarkable influence on the cyclization reactivity of 5-hexenyl radicals, leading to significant enhancement of their rate constants for 5-*exo* cyclization, as well as to an unexpected impact on the regiochemistry of such processes, a result not readily rationalized.[6]

In this paper, we present data for cyclizations of a series of fluorinated 5-hexenyl, 6-heptenyl, and 7-octenyl radical systems, including ethers, which provide considerable insight into the factors that govern cyclization reactivity and regiochemistry in such systems.[7]

Table 1. Cyclization Reactivities of Hydrocarbon Radicals at 25 °C[4,5]



	k_{exo}/s^{-1}	k_{endo}/s^{-1}
$n = 1$	2.7×10^5	5×10^3
$n = 2$	5.4×10^3	7.5×10^2
$n = 3$		1.2×10^2



Results

Absolute rate constants for the cyclizations of the series of fluorinated radicals **1**−**7** (see list in Table 2) were determined by uni- vs bimolecular competition experiments, as depicted for radical **2** in Scheme 1. Reactions were carried out under pseudo-first-order conditions designed so that kinetically controlled cyclizations of the intermediate radicals took place at a rate competitive with their abstraction of a hydrogen atom from a reduc-

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[||] Contribution No. 7938.

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(3) Fluorinated examples: (a) Morikawa, T.; Kodama, : Y.; Uchida, J.; Takano, M.; Washio, Y.; Taguchi, T. *Tetrahedron* **1992**, *41*, 8915. (b) Arnone, A.; Bravo, P.; Frigerio, M.; Viani, F.; Cavicchio, G.; Crucianelli, M. *J. Org. Chem.* **1994**, *59*, 459. (c) Arnone, A.; Bravo, P.; Viani, F.; Zanda, M.; Cavicchio, G.; Crucianelli, M. *J. Fluorine Chem.* **1996**, *76*, 169.
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(7) Some of this work has been reported previously in communication form: Dolbier, W. R., Jr.; Li, A. R.; Smart, B. E.; Yang, Z.-Y. *J. Org. Chem.* **1998**, *63*, 5687.

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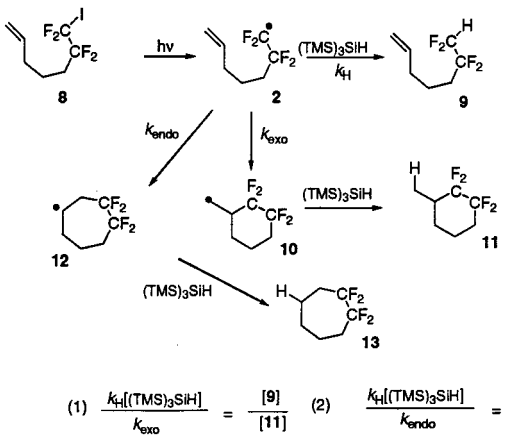
Table 2. Competition Rate Data for Cyclization versus Reduction of Fluorinated 5-Hexenyl, 6-Heptenyl, and 7-Octenyl Radicals, 1−7, at 25 ± 2 °C

compound	$k_H/k_c(exo)$	$k_H/k_c(endo)$[a]	red. agent	$k_H/10^6$ M^{-1} s^{-1} [a]
1, CH_2=$CHCH_2OCF_2CF_2$•	1.38 ± 0.04		$(TMS)_3SiH$	52 ± 6[b]
2, CH_2=$CH(CH_2)_3CF_2CF_2$•	1.25 ± 0.02	21.7 ± 0.5	$(TMS)_3SiH$	18 ± 1[c]
3, CH_2=$CHCH_2(CF_2)_3CF_2$•	2.56 ± 0.08		$(TMS)_3SiH$	51 ± 5[d]
4, CH_2=$CHCH_2O(CF_2)_2CF_2$•	0.41 ± 0.02		Et_3SiH	0.50 ± 0.04[e]
5, CH_2=$CHO(CH_2)_2CF_2CF_2$•	9.77 ± 0.23	27.1 ± 0.8	*n*-Bu_3SnH	92 ± 8[d]
6, CH_2=$CH(CH_2)_4CF_2CF_2$•		2.84 ± 0.14	$tBuMe_2SiD$	0.055 ± 0.0.013[d]
7, CH_2=$CH(CH_2)_2O_2CCF_2CF_2$•		3.28 ± 0.15	Et_3SiD	0.12 ± 0.01[b]

[a] For radicals **5**−**7**, the values are for k_D rather than k_H. [b] This work. [c] Reference 6. [d] Reference 11. [e] Reference 12. [f] Reference 10.

Scheme 1



ing agent. All of the competition studies except for those involving radicals, **6** and **7**, which were relatively unreactive toward cyclization, were carried out using C_6D_6 as solvent. To avoid complications from reactions of these radicals with the benzene solvent, 1,2-dichloroethane was used as solvent for these two radical systems.[8,9] Another tactic used to obtain more effective competitions in those two systems was to use the D-transfer agents *t*-$BuMe_2SiO$ and Et_3SiD, instead of the usual H-transfer analogues, to take advantage of the slower rates of D-transfer.[10]

Using the study of radical **2** in Scheme 1 as an explicit example, the ratios of products **11**:**9** and **13**:**9** were determined directly by ^{19}F NMR analysis of the product mixtures. The rate constants, k_{exo} and k_{endo}, were obtained by means of plots of experimental concentration data using eqs 1 and 2 in conjunction with the known values for k_H.

There was one required k_H value not yet known, that of hydrogen transfer from $(TMS)_3SiH$ by radicals of the type $ROCF_2CF_2$•. To obtain this H-transfer rate constant, an *absolute* rate constant for the addition of $ROCF_2CF_2$• to some alkene was needed, so that we could carry out an appropriate addition versus reduction competition study. The required values of k_{add} were obtained by 308 nm laser flash photolysis (lfp) of $CH_3OCF_2CF_2I$ in Freon 113 at 298 K in a manner described previously.[13] In this manner, values of k_{add} [2.08 (±0.2) × 10^8 M^{-1} s^{-1} and 3.10 (±0.3) × 10^7 M^{-1} s^{-1}] were obtained for addition of $CH_3OCF_2CF_2$• radical to α-methylstyrene and to pentafluorostyrene, respectively.

Table 3. Cyclization Rate Constants of Fluorinated 5-Hexenyl, 6-Heptenyl, and 7-Octenyl Radicals, 1−7, at 25 ± 2 °C

radical	% *exo* product	$k_c(exo)/10^6$ s^{-1}	$k_c(endo)/10^6$ s^{-1}	k_c/s^{-1} (model)[a]	k_{rel}[b]
1	>98	38 ± 4		8.5×10^6	4.5
2	94.5	14.4 ± 0.9		5.4×10^3	2667
		0.83 ± 0.05	7.5×10^2		1107
3	>98	19.9 ± 2		5.4×10^3	3685
4	>98	1.21 ± 0.12		(5.4×10^3)	224
5	73.4	9.4 ± 0.9		(5.4×10^3)	1740
			3.4 ± 0.3	(7.5×10^2)	4533
6	<2		0.020 ± 0.005	1.2×10^2	167
7	<2		0.036 ± 0.003	1.2×10^2	300

[a] Appropriate model radical system; in the case of **1**, a hydrocarbon ether model (ref 4); for all others, hydrocarbon models were used (ref 5). [b] k_c of radical versus k_c of model system.

It was then fortunately possible to devise a good competition experiment using pentafluorostyrene in competition with $(TMS)_3SiH$, wherein the rate constant k_H = 5.2 (±0.6) × 10^7 M^{-1} s^{-1} was obtained in a manner described previously.[12] This value is virtually identical to that for the analogous H-transfer to a perfluoro-*n*-alkyl radical [k_H = 5.1 (±0.5) × 10^7 M^{-1} s^{-1}].[11]

There remained one rate constant, k_D, in Table 2 for which there was not a measured value, that of reduction of the radical, $RO_2CCF_2CF_2$•, by Et_3SiD. Not having lfp data for alkene additions of this radical, we have arbitrarily chosen to use the k_D value [1.2 × 10^5 M^{-1} s^{-1}] for Et_3SiD's reaction with *n*-C_4F_9•.[14] Since radicals $R_FCF_2CF_2$• and $ROCF_2CF_2$• have identical reactivities and RCF_2CF_2• is only 2−3 times less reactive,[15,16] one can assume that a radical of the type $RO_2CCF_2CF_2$• will have a reactivity more similar to that of *n*-R_F• than to that of RCF_2CF_2•. Thus we have used the k_H value of *n*-R_F• to approximate the cyclization rate constant for radical **7**.

With all required values for k_H (or k_D) in hand along with the determined ratios of k_H/k_C (or k_D/k_C), it was therefore possible to calculate the values for k_{exo} and k_{endo} for each of the radical systems, **1**−**7**. These values are given in Table 3.

Two other radicals, **14** and **15**, were examined under conditions similar to those used for the less reactive systems, **6** and **7**, those being:

(8) 1,2-Dichloroethane has one of the smallest rate constants that has been measured for bimolecular H-transfer to a perfluoro-*n*-alkyl radical.[9]

(9) Shtarev, A. B.; Tian, F.; Smart, B. E.; Dolbier, W. R., Jr. *J. Am. Chem. Soc.* **1999**, in press.

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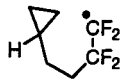
(14) This value was determined by a direct competition between Et_3SiH and Et_3SiD in their reaction with *n*-C_4F_9•, as described in the Experimental Section. k_H/k_D was determined to be 4.04 ± 0.13.

(15) 2.2 and 2.8 times less reactive with n-Bu_3SnH and $(TMS)_3SiH$, respectively.[16]

(16) Bartberger, M. D.; Dolbier, W. R., Jr.; Lusztyk, J.; Ingold, K. U. *Tetrahedron* **1997**, *53*, 9857.

$CH_2=CHOCH_2CH_2CH_2CH_2CF_2CF_2^{\bullet}$ 8-nonenyl system

14



a cyclopropane analog of a 5-hexenyl system

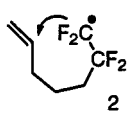
15

The latter was studied to determine whether a cyclopropane ring might act as an addend in an intramolecular reaction with a fluorinated radical. No cyclization products were observed for either of these radical systems under our experimental conditions, using *t*-$BuMe_2SiH$ as the H-transfer agent.

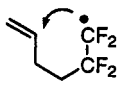
Discussion

This kinetic study of fluorinated 6-heptenyl and 7-octenyl radical cyclizations demonstrates that the earlier-observed significant enhancing influence of fluorine substituents on 5-hexenyl cyclization rate constants is manifested to an even greater extent within 6-heptenyl systems, with similar regiochemical variations being observed. Significant enhancements of *endo*-cyclizations of 7-octenyl systems are also observed. The single 8-nonenyl radical system that was examined failed to cyclize under our experimental conditions, and cyclization was found not to occur by addition to a cyclopropane ring in place of a double bond.

6-Heptenyl Radical Systems. The 6-*exo*-cyclizations of tetra- and octafluoroheptenyl radicals **2** and **3** occur with rate constants 3 orders of magnitude larger than that of their hydrocarbon analogue. To our surprise these rate constants are amazingly similar to those of the fastest 5-hexenyl radical cyclizations that we have reported.[6] For example, the total cyclization reactivity of tetrafluoro-6-heptenyl system **2** is slightly greater than that of tetrafluoro-5-hexenyl system, **16**,[6] and octafluoro-6-heptenyl system **3** is only 2.5 times less reactive than its most analogous 5-hexenyl system, **17**.[6]



2

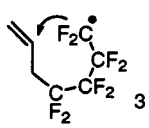


16

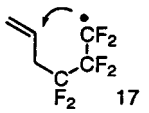
$k_{6\text{-exo}} = 1.4 \times 10^7\ s^{-1}$ $k_{5\text{-exo}} = 1.2 \times 10^7\ s^{-1}$

$k_2/k_{16} = 1.2$

The reason that 6-heptenyl systems **2** and **3** exhibit greater enhancements in cyclization rates (relative to the hydrocarbon systems) than 5-hexenyl systems **16** and **17** reflects the fact that, consistent with the reactivity–selectivity principle, slow reactions (i.e, 6-heptenyl cyclizations) should be more responsive to kinetically beneficial structural change than fast reactions (i.e., 5-hexenyl cyclizations). As it is, the cyclization rate constant of **3** is by far the largest yet measured for a 6-*exo* cyclization. Even the cyclization of 7,7-diphenyl-6-heptenyl radical, which forms a highly stabilized radical upon cyclization, has a rate constant of only $5 \times 10^5\ s^{-1}$, 40 times slower.[17]



3

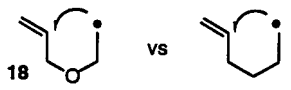


17

$k_{6\text{-exo}} = 2.0 \times 10^7\ s^{-1}$ $k_{5\text{-exo}} = 4.5 \times 10^7\ s^{-1}$

$k_3/k_{17} = 0.4$

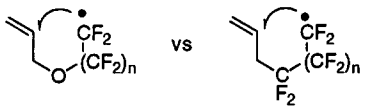
5-Hexenyl and 6-Heptenyl Ether Radical Systems. Beckwith earlier demonstrated that replacement of the C_3-methylene in the skeleton of the 5-hexenyl radical with an oxygen atom led to a significantly more reactive radical system, **18**, exhibiting a 5-*exo* cyclization rate constant ($8.5 \times 10^6\ s^{-1}$) 37 times greater than that of the parent, non-ether system.[4,18]



18 vs

$k_{rel} = 37$

Contrary to our expectations based on this result, when the C_4-CF_2 group of 6-heptenyl radical **3** was similarly replaced by an oxygen atom to give radical (**4**), cyclization was 10 times slower than for **3**. To determine whether this detrimental impact of **4**'s ether linkage was due to something intrinsic to the 6-heptenyl system, the reactivity of an analogous fluorinated 5-hexenyl ether, **1**, was examined. Indeed, ether radical **1** was found to also be less reactive toward cyclization than its non-ether analogue **17**. Therefore, both the 5-hexenyl and the 6-heptenyl fluorinated radicals **1** and **4**, which contained allylic ether linkages, failed to exhibit the enhanced reactivity that is characteristic of hydrocarbon ether radical systems, such as **18**.



1, n = 1 vs **17**, n = 1

4, n = 2 vs **3**, n = 2

$k_1/k_{17} = 0.8$

$k_4/k_3 = 0.06$

Why should the presence of an allylic ether linkage be beneficial to cyclization of hydrocarbon radical **18** but detrimental to the cyclizations of the hydrofluorocarbon radicals **1** and **4**? The answer probably comes from a combination of factors deriving from the impact of the allylic oxygen atom. First, there is the potential impact of the oxygen atom on the relative energies of ground state conformations, particularly the way in which it affects the mole fraction of what Bruice has termed "near attack conformations."[19] This must be considered an unknown factor at this time, since we have not yet calculated the pertinent conformational distributions. Second, it was suggested by Beckwith that the enhanced reactivity of ether **18** ($k_{rel} = 37$), as compared to its non-ether analogue, was the result of the impact of the oxygen atom on bond lengths and bond angles within **18**, so as to make its 5-*exo* cyclization transition state more easily

(17) Newcomb, M.; Horner, J. H.; Filipkowski, M. A.; Ha, C.; Park, S.-U. *J. Am. Chem. Soc.* **1995**, *117*, 3674.

(18) Beckwith, A. L. J.; Glover, S. A. *Aust. J. Chem.* **1987**, *40*, 157.

(19) Bruice, T. C.; Lightstone, F. C. *Acc. Chem. Res.* **1999**, *32*, 127.

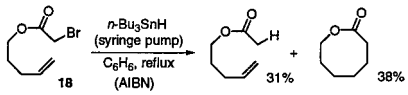
attained.[18] The present results certainly do not exclude such factors from playing a role for **18**, or for that matter for radicals **1** and **4**, but on the basis of our broad studies of fluorinated radical cyclizations, we have come to believe that polar influences may be the most important of the factors involved in *all* of these ether systems.

If the transition state for cyclization maintains the C−O bond in a geometry that will allow interactive overlap of the C−O σ^* orbital with the alkenyl π bond, such perturbation would be expected to lower the energies of both the HOMO and the LUMO of the alkenyl segment. In the case of the *nucleophilic* hydrocarbon ether radical **18**, such an effect would be beneficial to the cyclization transition state, because the allylic oxygen effectively makes the alkene segment more electrophilic. In contrast, for *electrophilic* fluorinated ether radical systems **1** and **4**, this same influence of the allylic oxygen should prove detrimental to cyclization. Thus, the different effect of a skeletal allylic oxygen atom on the rate constants for cyclization of a hydrocarbon versus a fluorohydrocarbon radical system can be explained simply in terms of the difference in the dipolar nature of their respective transition states.

It is interesting to note that when the ether linkage is vinylic rather than allylic, as in radical **5**, the 6-*exo* cyclization rate constant is only slightly less ($k_{rel} = 0.65$) than that of the non-ether analogue **2**, whereas its 7-*endo* cyclization rate constant is four times larger! The significant regiochemical influence of the vinyl ether group is undoubtedly a reflection of the greater ability of the oxygen atom of **5** to provide electrons to the 7-*endo*-cyclization transition state than to the 6-*exo* transition state. As a consequence, there is 27% *endo*-cyclization in the case of radical **5** but virtually none in the cyclization of closest non-ether analogue **3** (and only 5% in the cyclization of tetrafluoro radical **2**.)

Regiochemistry. Although continuing to display a greater propensity to undergo *endo*-cyclization than purely hydrocarbon systems, the 6-heptenyl systems **2** (5.5%) and **3** (<4%) exhibit a lesser tendency to undergo such addition than their 5-hexenyl analogues **16** (18%) and **17** (11%).[6] Although the data for the 6-heptenyl system are more limited, similar trends in *endo* vs *exo* reactivity seem to be observed for the 5-hexenyl and 6-heptenyl radical systems. For example, less *endo*-addition is observed when fluorine substitution extends to the homoallylic position (as in **3** and **17**) than for the situation (as in **2** and **16**) where the fluorine atoms inducing radical electrophilicity are more distant from the alkene site. Apparently, the impact of fluorines on regiochemistry results from two effects, the first relating to the structure and electrophilicity of the fluorinated radicals and the second relating to the influence of the neighboring fluorine substituents on the regiochemical reactivity of the double bond. A detailed theoretical examination of both the 5-hexenyl and 6-heptenyl fluorinated radical systems, currently nearing completion, will hopefully provide more definitive insight into the nature of these factors.

Cyclizations To Form Even Larger Rings. With the huge accelerations observed in cyclizations of the fluorinated 6-heptenyl radical systems **2** and **3**, it was hoped that similar, if not greater, enhancements would be observed for the 7-octenyl radical systems **6** and **7**. The latter system was examined in response to the recent report of a reasonably efficient 8-*endo* cyclization of (alkoxycarbony)methyl radicals, such as **18**,[1] using syringe pump addition of *n*-Bu_3SnH, conditions that maximize the potential efficiency of radical cyclization processes.



Unfortunately, although a significant enhancement (a factor of 167) was observed for the 8-*endo*-cyclization of 7-octenyl radical **6**, there was not the same order of magnitude of acceleration derived from its four fluorine substituents as there had been for analogous 6-heptenyl radical **2**. A slightly greater enhancement for 8-*endo*-cyclization of ester radical **7** (factor of 300) was observed. These observed exclusive 8-*endo*-cyclizations were unremarkable. Beckwith previously observed that the hydrocarbon 7-octenyl radical also cyclized in an exclusively 8-*endo* manner.[4] Apparently, Baldwin's rules do not apply in the formation of such large rings, and the thermodynamically more-stable cyclization product (from *endo*-addition) prevails.

In an attempt to measure the rate constant for cyclization of a fluorinated 8-nonenyl radical, a kinetic study of radical **14** using *t*-$BuMe_2SiH$ as competing hydrogen transfer agent led to *no* observable cyclization products (i.e., <2%). Thus it appears that, using our current competition kinetic methodology, the rates of 8-*exo*- or 9-*endo*-cyclizations of fluorinated radicals are too slow to be measured. We were also not able to detect the intramolecular 6-*exo*-cyclization onto the cyclopropane ring of radical **15**.

Conclusions

In conclusion, remarkably fast rates have been observed for 6-*exo*-cyclizations of partially fluorinated 6-heptenyl radicals **2** and **3**. The results are consistent with transition state polar influences being involved in the intramolecular addition of electrophilic fluorinated radicals to nucleophilic hydrocarbon alkene systems. The large observed unimolecular rate constants of such cyclizations make it likely that these processes will function quite efficiently as propagation steps in cyclopolymerization processes.[20]

Although similarly fluorinated 7-octenyl radicals do cyclize (in an *endo* manner) with measurable rate constants, the rates are considerably slower. Finally, fluorinated 8-nonenyl radicals were not observed to cyclize under the competition conditions used in this study.

Experimental Section

General. ^1H and ^{19}F NMR (300 and 282 MHz respectively) were measured in $CDCl_3$ using TMS as internal standard for ^1H and $CFCl_3$ or trifluorobenzene for ^{19}F. All reagents, unless otherwise specified, were purchased from Aldrich, PCR, or Synquest and used as received. Benzene was distilled from lithium aluminum hydride and stored over 4 Å molecular sieves; triglycol methyl ether (TG) was distilled from NaH. 1,1,2,2-Tetrafluoroethyl methyl ether has been synthesized and characterized previously.[21] Preparative gas chromatogra-

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phy was carried out on a 20 ft × 0.25 in. copper column packed with 20% SE-30 on Chromosorb P.

Synthesis of Partially-Fluorinated Radical Precursors. 1,1,2,2-Tetrafluoro-2-iodoethyl Methyl Ether. ICF_2CF_2I (3.54 g, 10 mmol) was added to sodium methoxide (0.54 g, 10 mmol) in 50 mL of TG at −78 °C, and then the mixture was warmed to room temperature in 20 min, with stirring continued for 18 h. The product was purified by preparative GC (1.93 g, 75%): ^{1}H NMR δ 3.68 (s, 3H); ^{19}F NMR δ −62.97 (s, 2F), −92.63 (s, 2F); HRMS calcd for $C_3H_3F_4IO$, 257.9165, found 257.9146.

1,1,2,2-Tetrafluoro-2-iodoethyl Allyl Ether (Precursor to Radical 1). ICF_2CF_2I (3.54 g, 10 mmol) was added to sodium allyloxide (0.8 g, 10 mmol) in 50 mL of TG at −20 °C, and the mixture was warmed to room temperature in 10 min, with stirring continued for 18 h. After workup, the product was purified by preparative GC to give 1,1,2,2-tetrafluoro-2-iodoethyl allyl ether (2.27 g, 80%): ^{1}H NMR δ 3.51 (d of t, 2H, J = 8 Hz, J = 2 Hz), 4.44 (m of d, 1H, J = 11 Hz), 4.56 (m of d, 1H, J = 17 Hz), 5.01 (m, 1H); ^{19}F NMR δ −62.20 (s, 2F), −88.50 (s, 2F); HRMS calcd for $C_5H_5F_4IO$, 283.9321, found 283.9321.

5,5,6,6-Tetrafluoro-6-bromohexanol. A total of 2.35 g (10 mmol) of 5,5,6,6-tetrafluoro-6-bromohexene and 0.11 g (2.9 mmol) of sodium borohydride were dissolved in 6 mL of dry triglyme under nitrogen atmosphere, $BF_3.OEt_2$ (0.57 g, 4.0 mmol) in 1 mL of triglyme was added dropwise to the mixture, and the mixture was stirred at room temperature for 1 h. To the resultant solution was added 1 mL of water to decompose excess sodium borohydride. Then 1.33 mL of NaOH (3 M) was added followed by the addition of 1.33 mL of 30% H_2O_2. The mixture was stirred for another 2 h and then poured into 40 mL of ice water and extracted with ethyl ether (3 × 100 mL). The combined ethereal extracts were washed with two 50 mL portions of water and dried over $MgSO_4$. The concentrated residue was distilled under reduced pressure to give 5,5,6,6-tetrafluoro-6-bromohexanol (2.0 g, 80% yield): bp 110 °C/30 mmHg; ^{1}H NMR δ 1.65 (m, 4H), 2.10 (m, 2H), 3.66 (t, 2H, J = 6 Hz); ^{19}F NMR δ −66.06 (s, 2F), −112.62 (t, 2F, J = 18 Hz); HRMS calcd for $C_6H_8BrF_4O$ (M^+ − 1), 250.9695, found 250.9656.

5,5,6,6-Tetrafluoro-6-bromohexanal. 5,5,6,6-Tetrafluoro-6-bromohexanol (10.12 g, 40 mmol) in 8 mL of CH_2Cl_2 was added to pyridium chlorochromate (12.90 g, 60 mmol) suspended in 80 mL of CH_2Cl_2. The mixture was stirred at room temperature for an additional 6 h and filtered through silica gel. Concentration of the solvent followed by fractional distillation at reduced pressure afforded 4.2 g of 5,5,6,6-tetrafluoro-6-bromohexanal (42% yield): bp 88 °C/ 30 mmHg; ^{1}H NMR δ 1.85 (m, 2H), 2.02 (m, 2H), 2.50 (t, 2H, J = 7 Hz), 9.70 (s, 1H); ^{19}F NMR δ −66.31 (s, 2F), −112.69 (t, 2F, J = 17 Hz); HRMS calcd for $C_6H_8BrF_4O$ (M^+ + 1), 250.9695, found 250.9689.

6,6,7,7-Tetrafluoro-7-bromoheptene (Precursor to Radical 2). Methyltriphenylphosphonium bromide (6.84 g, 19 mmol) was dissolved in 15 mL of anhydrous THF at 0 °C. Then 7.06 mL of a 2.5 M solution of butyllithium in hexane was added dropwise to the mixture, which was stirred for an additional 0.5 h at 0 °C. 5,5,6,6-Tetrafluoro-6-bromohexanal (4.02 g, 16 mmol) in THF (10 mL) was added dropwise to the mixture. After addition, the mixture was warmed to room temperature and stirred for an additional 6 h. The contents were poured into 50 mL of water and extracted with ethyl ether (3 × 100 mL). The combined ethereal extracts were washed with two 50 mL portions of water and dried over $MgSO_4$. The concentrated residue was purified by preparative GC to give 6,6,7,7-tetrafluoro-7-bromoheptene (1.59 g, 40% yield): ^{1}H NMR δ 1.69 (p, 2H, J = 8 Hz), 2.03−2.16 (m, 4H), 5.00−5.06 (m, 2H), 5.75 (m, 1H); ^{19}F NMR δ −65.47 (s, 2F), −111.92 (t, 2F, J = 18 Hz); HRMS calcd for $C_7H_9BrF_4$ 247.9824, found 247.9872.

4,4,5,5,6,6,7,7-Octafluoro-7-iodo-1-heptene (Precursor to Radical 3). Bis(tributyltin) (1.4 g, 2.43 mmol) was added to a 100 mL Pyrex tube in which allyl bromide (1.21 g, 10 mmol), 1,4-diiodo-perfluorobutane (4.54 g, 10 mmol), and benzene (50 mL) were charged. The mixture was degassed three times and sealed with a rubber septum under nitrogen and then photolyzed using a Rayonet reactor for 7 h. The product was purified by preparative GC (1.98 g, 54%): ^{1}H NMR δ 2.84 (d of t, 2H, J = 7 Hz, J = 18 Hz), 5.29−5.36 (m, 2H), 5.80 (m, 1H); ^{19}F NMR δ −58.90 (m, 2F), −113.33 (m, 2F), −113.83 (m, 2F), −122.69 (m, 2F); HRMS calcd for $C_7H_5F_7I$ (M^+ − F), 348.9324, found 348.9369.

1,1,2,2,3,3-Hexafluoro-3-iodopropyl Allyl Ether (Precursor to Radical 4). ICF_2CF_2COF (2.74 g, 10 mmol), allyl bromide (6.05 g, 50 mmol), and KF (2.90 g, 50 mmol) were mixed in TG (50 mL). The mixture was stirred at 80 °C for 1 day. After workup, the crude products were purified by preparative GC to obtain 1,1,2,2,3,3-hexafluoro-3-iodopropyl allyl ether (1.33 g, 40%): ^{1}H NMR δ 3.49 (d, 2H, J = 6 Hz), 4.40 (d of d, 1H, J = 11 Hz, J = 2 Hz), 4.51 (d of d, 1H, J = 17 Hz, J = 2 Hz), 4.96 (m, 1H); ^{19}F NMR δ −58.60 (m, 2F), −83.04 (s, 2F), −117.14 (m, 2F); HRMS calcd for $C_6H_5F_6IO$, 333.9289, found 333.9278.

4-Bromo-3,3,4,4-tetrafluorobutanoic acid was prepared according to the literature.[22]

3,3,4,4-Tetrafluoro-4-bromobutanol. $BH_3{\cdot}Me_2S$ (7.3 g, 0.096 mol) was added dropwise to $BrCF_2CF_2CH_2COOH$ (3.58 g, 0.015 mol) in 15 mL of THF at room temperature, and the mixture was then refluxed for 4 h. The reaction mixture was then poured into 40 mL of a saturated K_2CO_3 solution and extracted with ethyl ether (3 × 60 mL). The concentrated residue was distilled under reduced pressure (30 mmHg, 70 °C) to give 2.83 g (84% yield) of 3,3,4,4-tetrafluoro-4-bromobutanol: ^{1}H NMR δ 1.66 (s, 1H), 2.38 (t of t, 2H, J = 6 Hz, J = 18 Hz), 3.97 (t, 2H, J = 6 Hz); ^{19}F NMR δ −66.77 (s, 2F), −111.66 (t, 2F, J = 18 Hz).

3,3,4,4-Tetrafluoro-4-bromobutyl Vinyl Ether (Precursor to Radical 5). To a dry 45 mL of vinyl ethyl ether were added 1.9 g (8.44 mmol) of 3,3,4,4-tetrafluoro-4-bromobutanol and 1.49 g (4.67 mmol) of $Hg(OAc)_2$. The mixture was refluxed for 18 h. Then the mixture was diluted with hexane (100 mL) and washed sequentially with 5% NaOH, H_2O, and brine. The organic layer was dried over $MgSO_4$ and concentrated. Final purification by column chromatography gave 3,3,4,4-tetrafluoro-4-bromobutyl vinyl ether (0.84 g, 40% yield): ^{1}H NMR δ 1.97 (t of t, 2H, J = 6.6 Hz, J = 18 Hz), 3.44 (t, 2H, J = 6.6 Hz), 3.87 (d of d, 1H, J = 7 Hz, J = 2 Hz), 3.97 (d of d, 1H, J = 14 Hz, J = 2 Hz), 6.18 (d of d, 1H, J = 7 Hz, J = 14 Hz); ^{19}F NMR δ −66.46 (s, 2F), −111.08 (t, 2F, J = 18 Hz); HRMS calcd for $C_6H_7BrF_4O$, 249.9616, found 249.9608.

7,7,8,8-Tetrafluoro-8-bromooctene (Precursor to Radical 6). Fe (1.68 g, 30 mmol) and $CrCl_3{\cdot}6H_2O$ (1.06 g, 4 mmol) were mixed in 40 mL of EtOH, and then $BrCF_2CF_2Br$ (5.2 g, 20 mmol) and 1,5-hexadiene (2.05 g, 25 mmol) were added in one portion. The mixture was stirred at 65 °C for 14 h and then poured into 40 mL of 1 M HCl. The solution was extracted with CH_2Cl_2 (3 × 100 mL). The combined extracts were washed with two 50 mL portions of water and dried over $MgSO_4$. The concentrated residue was purified by preparative GC to give 7,7,8,8-tetrafluoro-8-bromooctene (1.5 g, 29% yield): ^{1}H NMR (C_6D_6) δ 0.95 (p, 2H, J = 7.5 Hz), 1.26 (m, 2H), 1.55−1.73 (m, 4H), 4.88−4.94 (m, 2H), 5.58 (m, 1H); ^{19}F NMR δ −66.01 (s, 2F), −112.55 (t, 2F, J = 18 Hz); HRMS calcd for $C_8H_{11}F_4Br$ 261.9980, found 261.9947.

3-Butenyl 3-iodo-2,2,3,3-tetrafluoropropionate (Precursor to Radical 7). 3-Iodo-2,2,3,3-tetrafluoropropionyl chloride (1.72 g, 5.91 mmol) was added dropwise to 3-buten-1-ol (0.72 g, 10 mmol) at 0 °C. After addition, the mixture was stirred for another 3 h. The usual workup gave the product which was purified by chromatography (1.21 g, 63%): ^{1}H NMR δ 2.43 (q, 2H, J = 6 Hz), 4.35 (t, 2H, J = 6 Hz), 5.06−5.12 (m, 2H), 5.70 (m, 1H); ^{19}F NMR δ −60.59 (t, 2F, J = 8 Hz), −111.78 (t, 2F, J = 8 Hz); HRMS calcd for $C_7H_7F_4IO_2$, 325.9427, found 325.9428.

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5,5,6,6-Tetrafluoro-6-bromohexyl Vinyl Ether (Precursor to Radical 14). To dry 54 mL of vinyl ethyl ether were added 2.53 g (10 mmol) of 5,5,6,6-tetrafluoro-6-bromohexanol and 1.77 g (5.55 mmol) of $Hg(OAc)_2$. The mixture was refluxed for 18 h, then diluted with hexane (100 mL), and washed sequentially with 5% NaOH, H_2O, and brine. The organic layer was dried over $MgSO_4$ and concentrated. The final purification by column chromatography gave 5,5,6,6-tetrafluoro-6-bromohexyl vinyl ether (1.00 g, 36% yield): ^{1}H NMR δ 1.72 (m, 4H), 2.10 (m, 2H), 3.69 (t, 2H, J = 5.7 Hz), 3.98 (d of d, 1H, J = 2.1 Hz, J = 6.6 Hz), 4.16 (d of d, 1H, J = 2.1 Hz, J = 14 Hz), 6.44 (d of d, 1H, J = 6.6 Hz, J = 14.1 Hz); ^{19}F NMR δ −66.10 (s, 2F), −112.64 (t, 2F, J = 19 Hz); HRMS calcd for $C_8H_{11}BrF_4O$, 277.9929, found 277.9882.

3,3,4,4-Tetrafluoro-4-bromobutylcyclopropane (Precursor to Radical 15). 5,5,6,6-Tetrafluoro-6-bromohexene (1.18 g, 5 mmol) was mixed with diazomethane in diethyl ether (from 5.1 g of diazald), then $Pd(OAc)_2$ (25 mg) was added in portions to the mixture, and the mixture was stirred for 10 min. Removal of the solvent afforded 1.02 g (82% yield) of 3,3,4,4-tetrafluoro-4-bromobutylcyclopropane: ^{1}H NMR (C_6D_6) δ 0.07 (m, 2H), 0.47 (m, 2H), 0.71 (m, 1H), 1.49 (m, 2H), 2.17 (m, 2H); ^{19}F NMR (C_6D_6) δ −66.06 (s, 2F), −112.09 (t, 2F, J = 18 Hz); HRMS calcd for $C_7H_9BrF_4$, 247.9824, found 247.9819.

Synthesis of Products from Kinetic Experiments. 1,1,2,2-Tetrafluoro-4-(2,3,4,5,6-pentafluorophenyl)butyl Methyl Ether. $CH_3OCF_2CF_2I$ (0.11 g, 0.43 mmol), Et_3SiH (0.23 g, 1.94 mmol), and 2,3,4,5,6-pentafluorostyrene (0.45 g, 2.33 mmol) were added to a Pyrex NMR tube. The mixture was degassed and photolyzed for 4 days; 80% of iodide was converted. The product was purified by preparative GC: ^{1}H NMR δ 2.25 (m, 2H), 2.96 (t, 2H, J = 7 Hz), 3.65 (s, 3H); ^{19}F NMR δ −94.75 (s, 2F), −119.28 (t, 2F, J = 18 Hz), −144.52 (d of d, 2F, J = 7 Hz, J = 22 Hz), −157.07 (t, 1F, J = 22 Hz), −162.88 (t of d, 2F, J = 22 Hz, J = 7 Hz); HRMS calcd for $C_{11}H_7F_9O$, 326.0353, found 326.0362.

1,1,2,2-Tetrafluoroethyl Allyl Ether. This product was also isolated by GC from the above reaction mixture: ^{1}H NMR δ 3.96 (d of t, 2H, J = 6 Hz, J = 2 Hz), 4.83−4.88 (m, 1H), 4.96 (m of d, 1H, J = 17 Hz), 5.05 (t of t, 1H, J = 54 Hz, J = 3 Hz), 5.47 (m, 1H); ^{19}F NMR δ −91.56 (m, 2F), −136.85 (d of t, 2F, J = 54 Hz, J = 5 Hz); HRMS calcd for $C_5H_6F_4O$, 158.0355, found 158.0357.

3-Methyl-4,4,5,5-tetrafluoro-1-oxacyclopentane. The same procedure was followed as for the preparation of 1-methyl-2,2,3,3,4,4,5,5-octafluorocyclohexane: ^{1}H NMR δ 0.52 (d, 3H, J = 7 Hz), 2.00 (m, 1H), 3.08 (m, 1H), 3.41 (m, 1H); ^{19}F NMR δ −78.08 (d, 1F, J = 139 Hz), −89.29 (d of d, 1F, J = 148 Hz, J = 12 Hz), −119.58 (d of t, 1F, J = 234 Hz, J = 12 Hz), −127.14 (d, 1F, J = 237 Hz); HRMS calcd for $C_5H_6F_3O$ (M^+ − F), 139.0371, found 139.0389.

6,6,7,7-Tetrafluoroheptene (9). 6,6,7,7-Tetrafluoro-7-bromoheptene (0.13 g, 0.51 mmol) and tris(trimethylsilyl)silane (0.17 g, 0.68 mmol) were dissolved in 1,3,5-trimethylbenzene (0.9 mL). The mixture was degassed and photolyzed for 6 h. 6,6,7,7-Tetrafluoroheptene was separated by GC: ^{1}H NMR (CD_3COCD_3) 1.59 (p, 2H, J = 8 Hz), 1.87−2.02 (m, 2H), 2.12 (q, 2H, J = 7 Hz), 4.91−5.02 (m, 2H), 5.69−5.83 (m, 1H), 6.12 (t of t, 1H, J = 53 Hz, J = 3.6 Hz); ^{19}F NMR δ −117.56 (t, 2F, J = 19 Hz), −137.0 (d, 2F, J = 53 Hz); HRMS calcd for $C_7H_{10}F_4$ 170.0719, found 170.0736.

1-Methyl-2,2,3,3-tetrafluorocyclohexane (11). The preparation method was the same as above: ^{1}H NMR (CD_3COCD_3) δ 1.07 (d, 3H, J = 6.9 Hz), 1.38 (m, 1H), 1.58 (m, 1H), 1.77−1.80 (m, 2H), 2.04−2.21 (m, 3H); ^{19}F NMR δ −115.26 (d of d, 1F, J = 33.8 Hz, J = 7.3 Hz), −116.15 (d of d, 1F, J = 34 Hz, J = 7.3 Hz), −119.38 (s, 1F), −120.27 (s, 1F); HRMS calcd or $C_7H_{10}F_4$ 170.0719, found 170.0731.

1,1,2,2-Tetrafluorocycloheptane (13). The preparation method was the same as above: ^{1}H NMR (CD_3COCD_3) δ 1.20 (m, 2H), 2.12 (m, 4H), 2.43 (m, 4H); ^{19}F NMR (CD_3COCD_3) δ −110.80 (m, 4F); HRMS calcd for $C_7H_{10}F_4$ 170.0719, found 170.0746.

4,4,5,5,6,6,7,7-Octafluoro-1-heptene. The mixture of $I(CF_2)_4CH_2CH{=}CH_2$ (0.21 g, 0.57 mmol) and Bu_3SnH (0.17 g, 0.57 mmol) in 1,2,4-trimethylbenzene (0.2 mL) was added to a Pyrex NMR tube and photolyzed for 0.5 h. The product was obtained by preparative GC: ^{1}H NMR δ 2.29 (d of t, 2H, J = 17 Hz, J = 6 Hz), 4.80 (d, 1H, J = 18 Hz), 4.90 (d, 1H, J = 10 Hz), 5.16 (t of t, 1H, J = 51 Hz, J = 5 Hz), 5.38 (m, 1H); ^{19}F NMR δ −113.67 (m, 2F), −125.53 (s, 2F), −130.32 (m, 2F), −137.47 (d, 2F, J = 51 Hz); HRMS calcd for $C_7H_6F_8$, 242.0342, found 242.0345.

1-Methyl-2,2,3,3,4,4,5,5-octafluorocyclohexane. AIBN (azo-bis-isobutyronitrile) (0.02 g, 0.14 mmol) was added to $I(CF_2)_4CH_2CH{=}CH_2$ (0.21 g, 0.57 mmol) in 0.5 mL of CH_2Cl_2. The solution was refluxed for 2 days to carry out an iodine transfer cyclization.[23] Then Bu_3SnH (0.17 g, 0.57 mmol) was added to the mixture, and it was photolyzed for 20 additional hours. The product was then purified by preparative GC: ^{1}H NMR δ 0.92 (d, 3H, J = 7 Hz), 1.60 (m, 1H), 2.18 (m, 1H), 2.65 (m, 1H); ^{19}F NMR δ −115.47 (m, F), −119.73 (d, 1F, J = 271 Hz), −125.60−126.93 (m, 3F), −130.82 (m, 1F), −143.86 (d, 1F, J = 102 Hz), −144.82 (d, 1F, J = 102 Hz); HRMS calcd for $C_7H_6F_8$, 242.0342, found 242.0365.

1,1,2,2,3,3-Hexafluoropropyl Allyl Ether. $ICF_2CF_2CF_2OCH_2CH{=}CH_2$ (0.21 g, 0.63 mmol) and Bu_3SnH (0.18 g, 0.63 mmol) were dissolved in 1,2,4-trimethylbenzene (0.2 mL). The solution was photolyzed for 0.5 h. The product was purified by preparative GC: ^{1}H NMR δ 3.43 (d of t, 2H, J = 6 Hz, J = 2 Hz), 4.36−4.47 (m, 2H), 4.81 (t of t, 1H, J = 51 Hz, J = 7 Hz), 4.92 (m, 1H); ^{19}F NMR δ −87.86 (m, 2F), −133.78 (m, 2F), −138.02 (d of t, 2F, J = 51 Hz, J = 7 Hz); HRMS calcd for $C_6H_6F_6O$, 208.0323, found 208.0323.

3-Methyl-4,4,5,5,6,6-hexafluoro-1-oxacyclohexane. AIBN (0.025 g, 0.16 mmol) was added to $I(CF_2)_3OCH_2CH{=}CH_2$ (0.21 g, 0.63 mmol) in CH_2Cl_2 (1 mL). The solution was refluxed for 2 days to carry out the iodine transfer cyclization.[23] Then Bu_3SnH (0.18 g, 0.63 mmol) was added to the mixture, and it was photolyzed for 20 h. The product was purified by preparative GC: ^{1}H NMR δ 0.41 (d of t, 3H, J = 7 Hz, J = 2 Hz), 1.56 (m, 1H), 2.67−2.74 (m, 1H), 2.87 (t, 1H, J = 12 Hz); ^{19}F NMR δ −89.37 (d of q, 1F, J = 17 Hz, J = 154 Hz), −93.62 (m of d, 1F, J = 154 Hz), −125.66 (d, 1F, J = 259 Hz), −128.59 (d, 1F, J = 281 Hz), −131.07 (m of d, 1F, J = 281 Hz), −131.07 (m of d, 1F, J = 281 Hz), −145.09 (d, 1F, J = 260 Hz); HRMS calcd for $C_6H_6F_6O$, 208.0323, found 208.0311.

3,3,4,4-Tetrafluorobutyl Vinyl Ether. $BrCF_2CF_2CH_2CH_2OCH{=}CH_2$ (0.10 g, 0.40 mmol) and Bu_3SnH (0.13 g, 0.45 mmol) were dissolved in 1,2,4-trimethylbenzene (1.5 mL). The solution was photolyzed for 8 h. The product was purified by preparative GC: ^{1}H NMR δ 2.44 (m, 2H), 3.97 (t, 2H, J = 6 Hz), 4.02 (d of d, 1H, J = 2 Hz, J = 7 Hz), 4.25 (d of d, 1H, J = 2 Hz, J = 14.4 Hz), 6.22 (t of t, 1H, J = 4.8 Hz, J = 53 Hz), 6.50 (d of d, 1H, J = 7 Hz, J = 14.4 Hz); ^{19}F NMR δ −117.26 (m, 2F), −137.63 (d, 2F, J = 53 Hz); HRMS calcd for $C_6H_8F_4O$, 172.0511, found 172.0553.

2-Methyl-3,3,4,4-tetrafluoro-1-oxacyclohexane. AIBN (0.025 g, 0.16 mmol) was added to $BrCF_2CF_2CH_2CH_2OCH{=}CH_2$ (0.16 g, 0.63 mmol) in 1 mL of CH_2Cl_2. The solution was refluxed for 2 days to carry out iodine transfer cyclization.[23] Then Bu_3SnH (0.18 g, 0.63 mmol) was added to the mixture, and it was photolyzed for 20 h. The product was purified by preparative GC: ^{1}H NMR δ 1.25 (d, 3H, J = 6 Hz), 2.29−2.38 (m, 2H), 3.67−3.82 (m, 2H), 4.02 (m, 1H); ^{19}F NMR δ −134.77 (d of m, 1F, J = 252 Hz), −137.43 (d, 1F, J = 257 Hz), −117.56 (d of m, 1F, J = 252 Hz), −120.46 (d, 1F, J = 257 Hz); HRMS calcd for $C_6H_8F_4O$, 172.0511, found 172.0501.

4,4,5,5-Tetrafluoro-1-oxacycloheptane. This product was also isolated by GC from the above reaction mixture: ^{1}H NMR δ 3.79 (t, 4H, J = 6 Hz), 2.38 (m, 4H); ^{19}F NMR δ −111.81 (m, 4F); HRMS calcd for $C_6H_8F_4O$, 172.0511, found 172.0536.

Kinetic Experiments

Determination of the Rate Constant for Addition of $CH_3OCF_2CF_2^\bullet$ to α-Methylstyrene and Pentafluorosty-

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rene by Laser Flash Photolysis of $CH_3OCF_2CF_2I$ in Freon 113 at 298 K. Values of k_{add} were determined by 308 nm laser flash photolysis (lfp) of $CH_3OCF_2CF_2I$ in Freon 113 at 298 K following procedures described in detail in our previous publications.[13] They were obtained as slopes of the plots of the observed rate constants for the growth of the absorption at ca. 320 nm of benzyl-like addition product radicals vs concentration of the styrene quencher.

Determination of the Rate Constant for H-atom Transfer to 1,1,2,2,-Tetrafluoro-2-methoxyeth-1-yl Radical from $(TMS)_3SiH$. Into each of a set of six Pyrex NMR tubes were added C_6D_6, 1-iodo-1,1,2,2-tetrafluoroethyl methyl ether, trifluorotoluene as an internal ^{19}F NMR standard, and varying amounts of $(TMS)_3SiH$ and 2,3,4,5,6-pentafluorostyrene. Each sample was sealed with rubber septa, frozen in a dry ice−2-propanol slush, and degassed (freeze and thaw) three times; then the tubes were photolyzed using a Rayonet reactor until the starting material was consumed completely. Product ratios for varied concentrations ratios of $(TMS)_3SiH/C_6F_5CH{=}CH_2$ allow the determination of the ratio k_H/k_{add}. Ratios of reduction and addition products were determined by the integration of the $-CF_2H$ and $-CF_2C_6F_5-$ (signals at δ −137.06 and −119.28, respectively) in the ^{19}F NMR. The hydrogen transfer rate constant $(5.2 \pm 0.6) \times 10^7$ M^{-1} s^{-1} was obtained on the basis of the addition rate constant of $ROCF_2CF_2^{\bullet}$ to 2,3,4,5,6-pentafluorostyrene $(3.1 \pm 0.3) \times 10^7$ M^{-1} s^{-1} as described previously.[16]

Competition of H versus D Abstraction from Triethylsilane and Triethylsilane-*d*. Determination of the Rate Constant for D-Transfer from Et_3SiD. The reactions were conducted in 1,3-bis(trifluoromethyl)benzene initiated with UV-light in Pyrex tubes. The overall concentration of the silanes was kept constant, and only their relative concentration was changed over the set of 6 tubes. Ratios of n-C_4F_9H/n-C_4F_9D were determined by the ratio of integrals of $-CF_2H$ and $-CF_2D$ resonances in the ^{19}F NMR at 138.7 and 139.4 ppm, respectively.

With a slope of 4.04 (±0.13), and using the known rate constant for k_H $(5.0 \pm 0.4 \times 10^5$ M^{-1} s^{-1}, a value of 1.2 (±0.1) $\times 10^5$ M^{-1} s^{-1} for k_D was calculated.

Competition Kinetics: Unimolecular Cyclization vs Hydrogen Atom Abstraction. General Procedure for Competition Studies. Into each of a set of six Pyrex NMR tubes were added C_6D_6 or dichloroethane, iodide, trifluorotoluene as an internal ^{19}F NMR standard, and varying amounts of hydrogen atom donors. Each sample was sealed with rubber septa, frozen in a dry ice−2-propanol slush, and degassed (freeze and thaw) three times; then the tubes were photolyzed using a Rayonet reactor until the starting material was consumed completely. Product ratios for varied concentrations of hydrogen atom donor allow the determination of the ratio $k_H/k_{exo(endo)}$ applying eqs 1 and 2. Yields are determined by integration of product resonances versus that of internal standard (δ −63.24) in the ^{19}F NMR spectrum.

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Supporting Information Available: Tables of raw kinetic data and ^1H and ^{19}F NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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