Syntheses of *F*-Adamantyl Polychlorides and *F*-1-Norbornyl Chloride: The First Documented 1,3-Chlorine Shift

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1,2-Dichloro-*F*-adamantane, 1,3-dichloro-*F*-adamantane, 1,3,5-trichloro-*F*-adamantane, 1,3,5,7-tetrachloro-*F*-adamantane, and 1-chloro-*F*-norbornane have been synthesized by aerosol direct fluorination from their corresponding hydrocarbons for the first time. All compounds have been characterized by ^{19}F NMR, FT-IR, mass spectrometry, and elemental analysis. The aerosol direct fluorination of 2,2-dichloroadamantane produced a mixture of two dichloro-*F*-adamantanes plus a trace amount of 2-chloro-*F*-adamantane (chlorine loss product). The mixture of dichlorinated products indicated that chlorine shifts during this aerosol direct fluorination had occurred. The high probability of a 1,3-chlorine shift versus sequential 1,2-chlorine shifts or intermolecular chlorine redistribution is discussed.

Introduction

Adamantane has interested chemists for nearly a century; research based on its unusual chemical and physical properties has led to important advances in several areas of organic chemistry.[1,2] Many adamantane derivatives such as adamantanone,[3] chlorinated adamantanes,[4,5] and 1,2-disubstituted adamantanes[6] have been synthesized. Some adamantane derivatives have even found applications in medicine.[7] However, far fewer fluorinated adamantane derivatives are known. We have been interested in preparing new perfluorodiamondoid compounds for several years and have reported successful syntheses of *F*-adamantane,[8] *F*-diamantane,[9] and *F*-adamantanone[10] by aerosol direct fluorination without rearrangement or fragmentation of the hydrocarbon frameworks, which is a particularly important consideration in diamondoid compounds.

Aerosol direct fluorination is a process in which vaporized organic reactants (injected into the evaporator as a pure liquid or as a solution in a co-fluorinating solvent using a syringe pump) are condensed/adsorbed onto aerosolized sodium fluoride particulates and reacted with dilute fluorine gas. The reaction of aerosol particulates and fluorine occurs initially in the dark at −10 to 0 °C; aerosolized particulates pass into a UV-irradiated transparent tube where reaction with fluorine is completed with little fragmentation or rearrangement. This predominantely free radical process has been previously applied to the synthesis of perfluorinated alkyl chlorides. 1,2-Chlorine shifts were observed during fluorination of secondary and tertiary alkyl chlorides.[11,12] In our previous work, most alkyl chlorides were limited to monochlorinated noncyclic compounds. The aerosol direct fluorination of 1-chloroadamantane and 2-chloroadamantane produced perfluorinated analogues in good yield with no 1,2-chlorine shift or chlorine loss.[13] This encouraged us to look more extensively into the aerosol direct fluorination of other adamantyl chlorides as a means by which preselected survivable sites for subsequent reaction could be incorporated into organic molecules prior to their fluorination. Additionally, the unique stereochemistry of the adamantane molecule has provided a template for mechanistic probing of aerosol direct fluorination. In this paper, the aerosol direct fluorinations of five chlorinated adamantanes and of 1-chloronorbornane are described. The unusual chlorine shift that occurs during aerosol direct fluorination of 2,2-dichloroadamantane is presented and discussed.

Results and Discussion

With the help of spectroscopic techniques (vide infra), the major products (90–95% by weight) collected from the aerosol direct fluorination of 1,2-dichloroadamantane, 1,3-dichloroadamantane, 1,3,5-trichloroadamantane, 1,3,5,7-tetrachloroadamantane, and 1-chloronorbornane were identified as their corresponding perfluorinated compounds with no chlorine loss or chlorine shift. The percent yields of 1,2-dichloro-*F*-adamantane, 1,3-dichloro-*F*-adamantane, 1,3,5-trichloro-*F*-adamantane, 1,3,5,7-tetrachloro-*F*-adamantane, and 1-chloro-*F*-norbornane based on the throughput (amounts injected) are 38.4%, 40.2%, 38.3%, 59.4%, and 51.9%, respectively. The aerosol direct fluorination of 2,2-dichloroadamantane produced a trace amount of 2-chloro-*F*-adamantane (1.2%, GLC, chlorine loss product), an inseparable mixture of two dichloro-*F*-adamantane isomers (90.7%), and one partially fluorinated 2,2-dichloroadamantane (8.1%). The combined percent yield of the latter three products based on the throughput is 55.4%. The aerosol system is dependent on the generation of a particulate aerosol that is ideally crystalline, monodisperse, and with little tendency to aggregate. In reality, only a few compounds produce near perfect aerosols exhibiting all of the previous properties. Most compounds that produce excellent aerosols are highly symmetrical and pack well in a crystal lattice. This could be one reason why the isolated percent yields of above products decreased somewhat as the symmetry of compounds decreased.

(1) Fort, R. C.; Schleyer, P. v. R. *Chem. Rev.* **1964**, *64*, 277.
(2) Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 3189.
(3) Schleyer, P. v. R.; Nicholas, R. D. *J. Am. Chem. Soc.* **1961**, *83*, 182.
(4) Stetter, H.; Krause, M.; Last, W. D. *Chem. Ber.* **1969**, *102*, 3357.
(5) Bach, R. D.; Badher, R. C. *Synthesis* **1979**, 529.
(6) Abdel-Sayed, A. N.; Bauer, L. K. *Tetrahedron* **1988**, *44*, 1873.
(7) Wishnok, J. S. *J. Chem. Educ.* **1973**, *50*, 780.
(8) Adcock, J. L.; Robin, M. L. *J. Org. Chem.* **1983**, *48*, 3128.
(9) Adcock, J. L.; Luo, H. *J. Org. Chem.* **1992**, *57*, 2162.
(10) Adcock, J. L.; Luo, H. *J. Org. Chem.* **1992**, *57*, 4297-4300.
(11) Adcock, J. L.; Evans, W. D.; Heller-Grossman, L. *J. Org. Chem.* **1983**, *48*, 4953.
(12) Adcock, J. L.; Evans, W. D. *J. Org. Chem.* **1984**, *49*, 2719.
(13) Adcock, J. L.; Luo, H.; Zuberi, S. S. *J. Org. Chem.* **1992**, *57*, 4749-4752.

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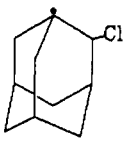
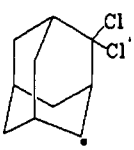
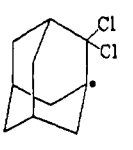
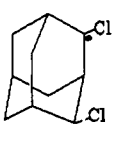
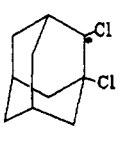
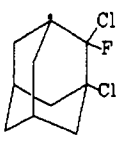
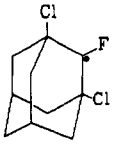
Table I. Heat of Formation for Some Intermediate Radicals Calculated by AM1[15]

	radical							
								
	A	B	C	D	E	F	G	H
ΔH_f (kcal/mol)	-17.2	-12.8	-18.6	-12.8	-29.0	-27.0	-51.0	-68.0

Generally, primary alkyl chlorides can be fluorinated to their perfluorinated analogues in good yield. Secondary alkyl chlorides produce a mixture of primary and secondary perfluorinated alkyl chlorides due to 1,2-chlorine shifts which may occur more than once during fluorination. Tertiary alkyl chlorides undergo complete rearrangement to primary alkyl and occasionally some secondary products especially when the secondary products are necessary intermediate products.[14] In contrast, no chlorine shifts were observed in aerosol direct fluorinations of 1-chloronorbornane or any of the chloroadamantanes investigated here except 2,2-dichloroadamantane. This phenomenon was initially attributed to the rigidity of the adamantane skeleton.[13] In order to understand more deeply the lack of a chlorine shift during the fluorination of adamantyl chloride, the heats of formation (listed in Table I) for some intermediate radicals were calculated by AM1 (Austin Model 1), a new general purpose semiempirical quantum mechanical molecular model based on the MNDO approximation.[15] The program has been optimized for heat of formation calculations of both neutral, closed-shell molecules and open-shell molecules[16] and has been extended to molecules containing halogen atoms.[17] The average errors for a large number of halogenated compounds is about 4.4 kcal/mol.[17] We believe that relative errors within a very closely related group of compounds such as the adamantanes should be better than this. If we consider 1-chloroadamantane as an example, Table I shows that the heat of formation (-17.2 kcal/mol) for radical A (a secondary radical), which was considered to be directly generated in the first few steps of this fluorination, is more stable than the heat of formation (-12.8 kcal/mol) for radical B (a tertiary radical). Since radical B is the 1,2-chlorine shift product of radical A, it is clearly seen that there is no thermodynamic driving force for the 1,2-chlorine shift of radical A to radical B. However even the reverse reaction, aerosol fluorination of 2-chloroadamantane, which should have a small thermodynamic driving force, does not occur. This lack of rearrangement has been further demonstrated during aerosol direct fluorinations of other bridgehead polychlorinated adamantanes. A kinetic reason is a better explanation for no 1,2-chlorine shift; the position of the C–Cl bond in radicals A and B precludes a 1,2-chlorine shift. Specifically, the p orbital occupied by the unpaired electron in radical A is oriented orthogonal to the C–Cl bond (see Figure 1), i.e., a 90° dihedral angle exists, the worst possible angle, one which maximizes the activation energy required

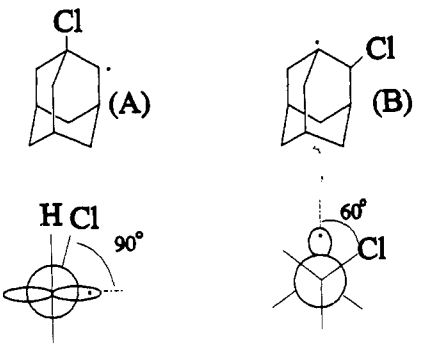


Figure 1. Radicals A and B.

for the 1,2-chlorine shift. Additionally the adamantane framework is so rigid that a twisted transition state connecting radical A and radical B should be energetically highly unfavorable. Aerosol direct fluorinations of 2-chloroadamantane and 1-chloronorbornane giving the perfluorinated analogues without chlorine shift can also be explained kinetically. In these two cases, the dihedral angle is 60° which is almost as bad as 90°.

The mixture of dichloro-*F*-adamantane isomers formed during the aerosol fluorination of 2,2-dichloroadamantane was composed of 2,2-dichloro-*F*-adamantane (80%, non-shift product) and another dichloro-*F*-adamantane (20%, chlorine shift product). In order to identify the second (rearranged) isomer, both 1,2-dichloroadamantane and 1,3-dichloroadamantane were prepared and fluorinated. It was clear from the ^{19}F NMR spectra that only the corresponding perfluorinated analogues were isolated; no chlorine shift was observed in either of these two cases. Comparison of ^{19}F NMR spectra (Figure 2) of 1,2-dichloro-*F*-adamantane and 1,3-dichloro-*F*-adamantane with that of the mixture of dichloro-*F*-adamantanes suggested that the rearranged product was neither 1,2-dichloro-*F*-adamantane nor 1,3-dichloro-*F*-adamantane. The remaining possibility, 2,4-dichloro-*F*-adamantane (3 isomers) was supported by the ^{19}F NMR spectrum (Figure 2). Now the question is how 2,4-dichloro-*F*-adamantane (3 isomers) could be formed during the aerosol direct fluorination of 2,2-dichloroadamantane. A possible mechanism for this fluorination is proposed in Schemes I and II. In radical D (similar to radical B in Figure 1) the dihedral angle of 60° is highly unfavorable for an intramolecular 1,2-chlorine shift to radical F, although radical F is 14.2 kcal/mol more stable than radical D. The overall unfavorableness of rearrangement is supported by the fact that no 1,2-dichloro-*F*-adamantane was obtained from the aerosol direct fluorination of 2,2-dichloroadamantane. Since any intramolecular 1,2-shift should be strongly inhibited just

(14) Evans, W. D. Ph.D. Dissertation, The University of Tennessee at Knoxville, Dec 1983.
(15) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
(16) Nelsen, S. F. *J. Chem. Soc., Perkin Trans. II* **1988**, 1005–1008.
(17) Dewar, M. J. S.; Zoebisch, E. G. *J. Mol. Struct. (Theochem)* **1988**, *180*, 1–21.

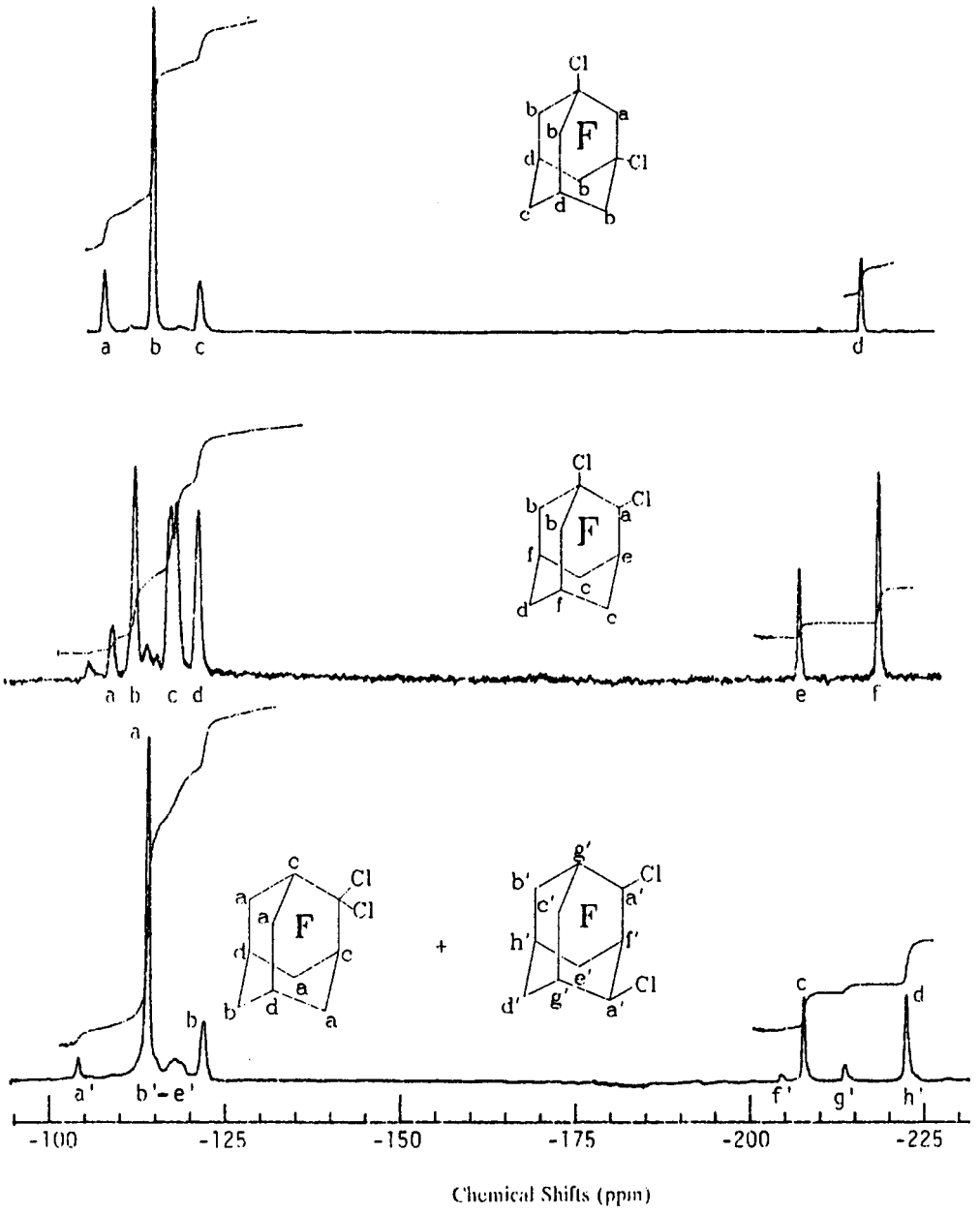


Figure 2. ^{19}F NMR spectra of 1,3-dichloro-*F*-adamantane, 1,2-dichloro-*F*-adamantane, and the mixture of two dichloro-*F*-adamantanes.

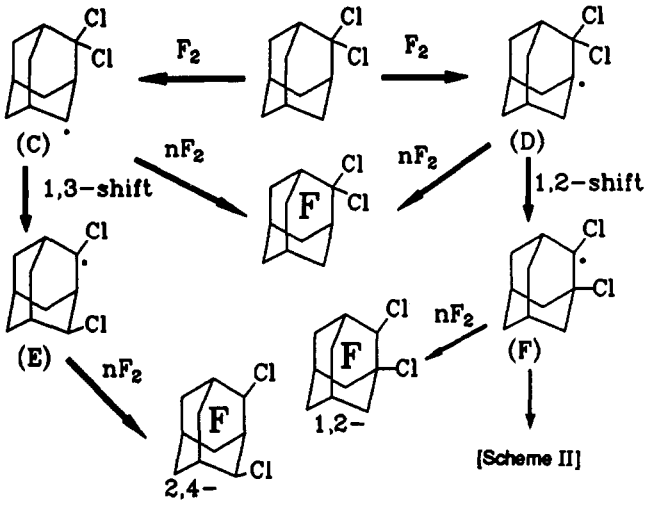
as are 1,2-hydride shifts on the adamantane nucleus,[18] the question becomes does the isomerization occur via intramolecular 1,3-chlorine shift or via an intermolecular process. Because only a trace amount of monochloro-*F*-adamantane was obtained and no trichloro or more highly chlorinated *F*-adamantanes were detected, the intermolecular process can be excluded. The calculated heat of formation in Table I indicates that radical C is more stable than radical D by 5.8 kcal/mol. The formation of radical C is also statistically more probable than radical D (8:2). Unlike noncyclic systems where the tertiary radical is usually more stable than the secondary radical or the primary radical because of hyperconjugation, the tertiary radical is less stable than the secondary radical in these tricyclic systems since the tertiary radical cannot become planar. Radical rearrangements should be most facile when the p orbital occupied by one electron and the C–Cl bonds are coplanar, i.e., the dihedral angle is 0°. This is exactly the case for a 1,3-chlorine shift from radical C to radical E (Figure 3) which when coupled with the 10.4 kcal/mol driving force for the rearrangement should be feasible. Radical E leads to 2,4-dichloro-*F*-adamantane (3 isomers) on further fluorination. From the above discussion we may conclude that a 1,3-chlorine shift has occurred during the aerosol direct fluorination of 2,2-dichloroadamantane. This appears to be the first documented example of a 1,3-chlorine shift.[19]

In order to confirm a 1,3-chlorine shift, the mixture of dichloro-*F*-adamantane isomers was converted into their dihydryl-*F*-adamantane isomers with tributyltin hydride. Unlike the dichloro-*F*-adamantane isomers, the dihydryl-*F*-adamantane isomers can be separated on a Fluorosilicone QF-1 column with the temperature program 120 °C, 28 min; 20 °C/min to 160 °C. The isomers were identified as 2,2-dihydryl-*F*-adamantane (t_R = 21.9 min, 79.0%), 2,4-

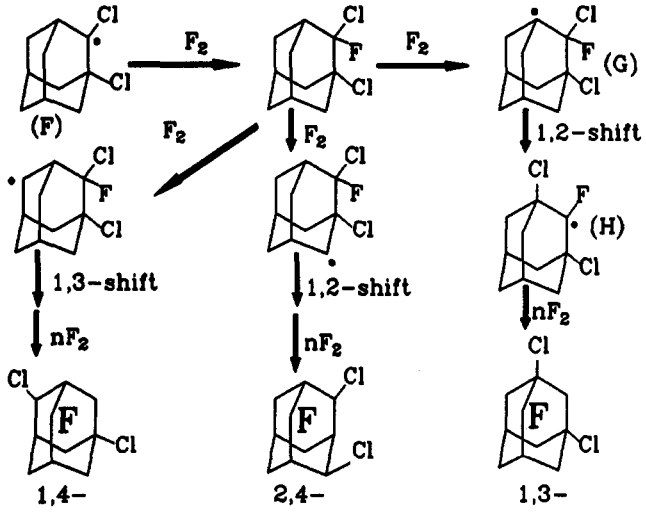
(18) Schleyer, P. v. R.; Lam, L. K. M.; Raber, D. J.; Fry, J. L.; McKervey, M. A.; Alford, J. R.; Cuddy, B. D.; Keizer, V. G.; Geluk, H. W.; Schlatmann, J. L. M. A. *J. Am. Chem. Soc.* **1970**, *92*, 5246.

(19) March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley & Sons, Inc.: New York, 1985; p 958.

Scheme I



Scheme II



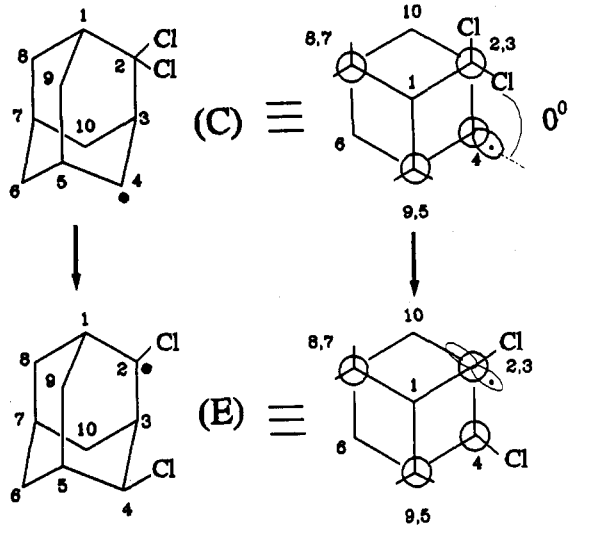


Figure 3. 1,3-Chlorine shift of radical C to radical E.

dihydryl-*F*-adamantane (3 isomers, t_R = 24.8 min, 13.7%), and possible 2-hydryl-4-chloro-*F*-adamantane (isomers, t_R = 41.5 min, 7.3%). The mass spectra of these dihydryl-*F*-adamantane isomers are similar. The most intense peak is that of the molecular ion minus HF which is common for other hydryl-*F*-adamantanes.[13] However, their ^{19}F NMR spectra are markedly different (see Figure 4). The ^{19}F NMR spectrum of 2,2-dihydryl-*F*-adamantane consisted of four unresolved peaks at −122.28, −124.35, −205.68, and −224.00 ppm (intensity 2:8:2:2), the first two are in the CF_2 region and the last two are in the CF region which is similar to that of 2,2-dichloro-*F*-adamantane. Its ^1H NMR spectrum had a peak at 2.67 ppm. The ^{19}F NMR spectrum of the 2,4-dihydryl-*F*-adamantane isomers had peaks at −120.68, −123.37, −204.71, −213.78, −215.17, −220.75, −224.25, and −225.41 ppm. Their ^1H NMR spectrum had an expected doublet of multiplets at 5.18 ppm (J_{HF} = 47.50 Hz). The complicated ^1H and ^{19}F NMR spectra of 2,4-dihydryl-*F*-adamantane suggests that it could be a mixture of $2_{ax},4_{eq}$-dihydryl-*F*-adamantane (a, in Figure 4), $2_{ax},4_{ax}$-dihydryl-*F*-adamantane (b, in Figure 4) and $2_{eq},4_{eq}$-dihydryl-*F*-adamantane (c in Figure 4). It is difficult to predict if these stereoisomers come directly from the corresponding 2,4-dichloro-*F*-adamantane stereoisomers or are produced by rearrangement of one specific 2,4-dichloro-*F*-adamantane since both processes are free radical in nature. Free radicals are ideally planar and attack from either side cannot be ruled out. This further substantiates that the chlorine-shift rearranged isomer is not the 1,2-dichloro-, the 1,3-dichloro-, or the 1,4-dichloro-*F*-adamantane isomer. Steric crowding of the two geminal chlorine atoms on the 2,2-dichloroadamantane and the greater stabilization of free radicals by chlorine relative to hydrogen[20] are other reasons why a 1,3-chlorine shift occurs during the fluorination of 2,2-dichloroadamantane. However, a 1,3-chlorine shift must be generally unfavorable; otherwise rearrangement should be observed during the fluorination of 1,2-dichloroadamantane, i.e., 1,4-dichloro-*F*-adamantane should be isolated, but none is observed.

Experimental Section

The aerosol fluorination reactor design and description together with a detailed operational procedure appear elsewhere.[21] The specific fluorination conditions for each compound are available in Table II. 1,2-Dichloroadamantane,[6] 1,3-dichloroadamantane,[4] 1,3,5-trichloroadamantane,[4] 1,3,5,7-tetrachloroadamantane,[5] and 2,2-dichloroadamantane[22] were synthesized by literature procedures and purified by column chromatography (silica gel, hexanes) wherever necessary. 1-Chloronorbornane was prepared from 2,2-dichloronorbornane which was made from norcamphor.[23] All starting materials were identified by ^1H and ^{13}C NMR spectra. The fluorinated products were manipulated on the vacuum line; some purifications could be achieved by fractionation using slush baths, but where needed GC [Bendix 2300, subambient multicontroller, equipped with a QF-1 column, 7 m × 3/8 in. 13% fluorosilicone QF-1 (Analabs) stationary phase on 60–80 mesh, acid washed Chromosorb P conditioned at 225 °C (12 h)] was used for purification. The purity of some of the compounds was monitored on a capillary GC (Hewlett-Packard 5890A) using a Supelco SP 2100 60 m × 0.25 mm i.d. fused silica column. Infrared spectra were recorded on a Bio-Rad Spc 3200 spectrophotometer. ^{19}F NMR spectra were observed using a JEOL FX 90Q (Omniprobe) as solutions in $CFCl_3$ which functioned as both solvent and internal standard. ^1H and ^{13}C NMR were recorded on a Bruker AC-250 NMR spectrometer equipped with a 5-mm switchable $^1H/^{13}C$ probe, the operating frequency for ^{13}C NMR being 62.89 MHz. The negative chemical

(20) Adcock, J. L. in *Synthetic Fluorine Chemistry*; Olah, G. A., Chambers, R. D., Prakash, G. K. S., Eds.; John Wiley & Sons, Inc.: New York, 1992; p 132.
(21) Adcock, J. L.; Cherry, M. L. *Ind. Eng. Chem. Res.* **1987**, *26*, 208.
(22) Cuddy, B. D.; Grant, D.; Karim, A.; McKervey, M. A.; Rea, E. J. F. *J. Chem. Soc., Perkin Trans. I* **1972**, 2701.
(23) Ward, G. A.; Bower, B. K.; Findlay, M.; Chien, C. W. *Inorg. Chem.* **1974**, *13*, 614.

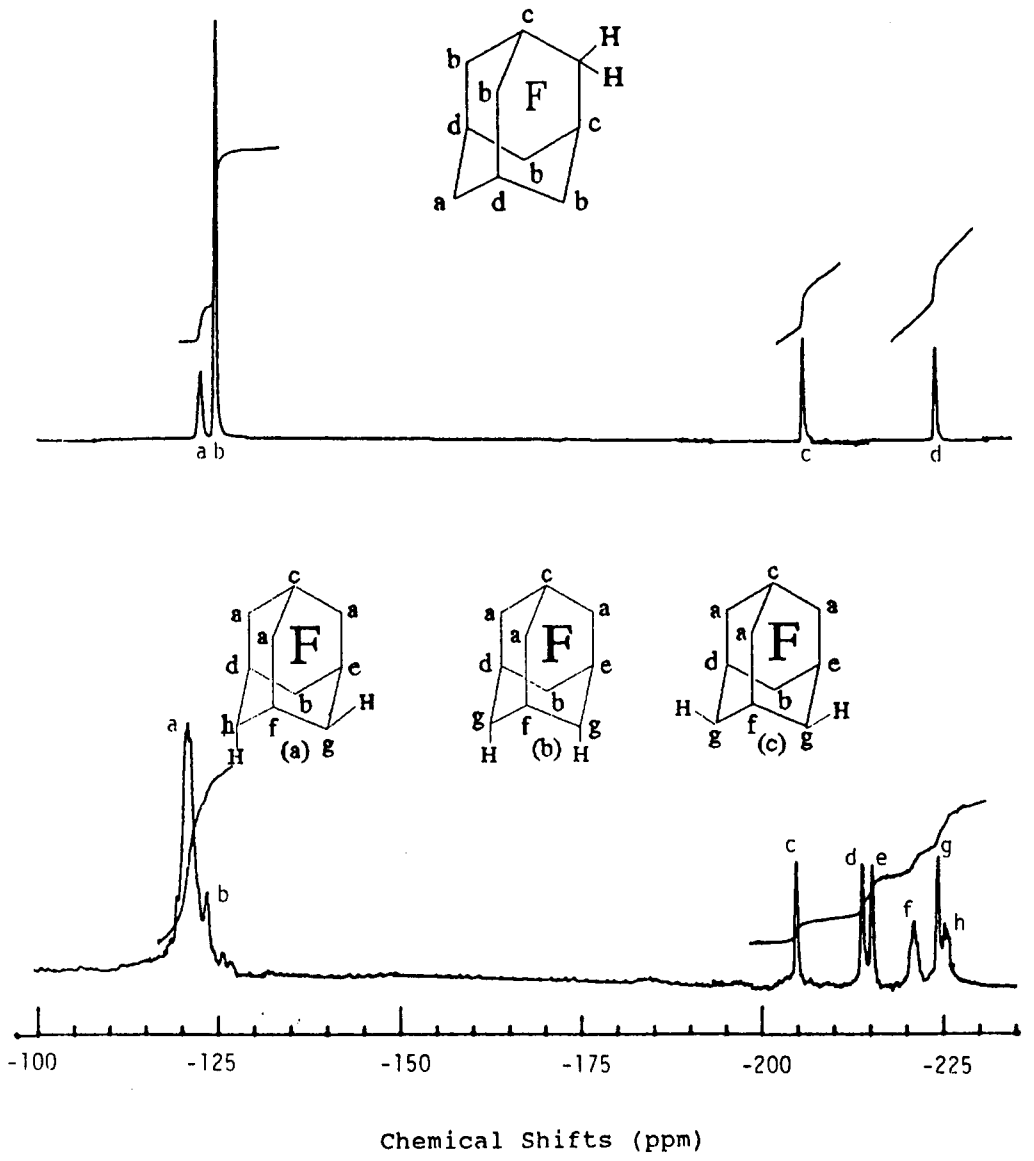


Figure 4. ^{19}F NMR spectra of 2,2-dihydryl-, and 2,4-dihydryl-*F*-adamantanes.

ionization (electron attachment) mass spectra were carried out on a VG ZAB-EQ mass spectrometer. Samples were introduced into the source via the reference inlet to a pressure of 10^{-6} Torr, diluted with nitrogen gas to 10^{-5} to 10^{-4} Torr, and bombarded with 70-eV electrons. The elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY.

The calculations were performed by the standard AM1 semiempirical SCF-MO method as implemented in the AMPAC program. The calculations were run using the unrestricted Hartree–Fock method. All equilibrium geometries were determined by minimizing the total energy with respect to all geometrical parameters using the standard Davidson–Fletcher–Powell procedure.[15]

(1) Aerosol Fluorination of 2,2-Dichloroadamantane. 2,2-Dichloroadamantane (2.13 g, 10.4 mmol) was fluorinated as a solution in 1,2,3-trichloropropane (10.04 g, 68.1 mmol) over a period of 5.83 h. A white solid (2.62 g, 5.74 mmol) was collected in the −22 °C trap and 1,2,3-trichloro-*F*-propane (10.7 g, 45.1 mmol) in the −78 °C trap. The contents of the −22 °C trap were dissolved in R-113 and separated on a Fluorosilicone QF-1 column (7 m × $^3/_8$ in.) with the temperature program 155 °C, 2 min; 1 °C/min to 175 °C, 8 min; 5 °C/min to 190 °C. The products were identified as 2-chloro-*F*-adamantane (t_R = 11.5 min, 1.2%), a mixture of dichloro-*F*-adamantane isomers (t_R = 18.2 min, 90.7%), and 4-hydryl-2,2-dichloro-*F*-adamantane (t_R = 27.9 min, 8.1%). The combined percent yield of these three compounds based on injection of 2,2-dichloroadamantane was 55.4% and the percent yield of 1,2,3-trichloro-*F*-propane based on injection of 1,2,3-trichloropropane was 66.2%. The ^{19}F NMR spectrum of the mixture of two dichloro-*F*-adamantane isomers showed that it consisted of 2,2-dichloro-*F*-adamantane (80%) which had four unresolved peaks at −113.89, −121.74, −207.67, and −222.37 ppm (integral 8:2:2:2) and 2,4-dichloro-*F*-adamantane (20%) which had peaks at −104.07, −117.25, −204.27, −213.50, and −222.50 ppm. The tentative assignments are shown in Figure 2. The mass spectrum showed the following peaks: [*m*/*z* (formula, intensity)] 423 ($C_{10}F_{14}{}^{37}Cl$, 6.7), 421 ($C_{10}F_{14}{}^{35}Cl$, 24.5), 404 ($C_{10}F_{13}{}^{37}Cl$, 14.2), 402 ($C_{10}F_{13}{}^{35}Cl$, 50), 387 ($^{13}CC_9F_{14}$, 13.2), 386 ($C_{10}F_{14}$, 100), and 367 ($C_{10}F_{13}$, 75). Anal. Calcd for $C_{10}F_{14}Cl_2$: C, 26.28; F, 58.20, Cl, 15.52. Found: C, 26.52; F, 58.05; Cl, 15.32. The vapor-phase infrared spectrum had absorption bands at 1302 (sh), 1286 (s), 1261 (s), 1241 (sh), 1198 (w), 1116 (w), 1030 (m), 976 (s), 943 (s), 882 (w), 862 (m), 789 (s), and 761 (s) cm^{-1}.

(2) Aerosol Fluorination of 1,2-Dichloroadamantane. 1,2-Dichloroadamantane (1.11 g, 5.41 mmol) was fluorinated as a solution in 1,2,3-trichloropropane (6.32 g, 47.4 mmol) over a period of 4.0 h. 1,2-Dichloro-*F*-adamantane (0.95 g, 2.07 mmol) was collected in the −22 °C trap and 1,2,3-trichloro-*F*-propane (7.89 g, 33.1 mmol) in the −78 °C trap. The percent yield of 1,2-dichloro-*F*-adamantane based on injection of 1,2-dichloroadamantane was 38.4% and the percent yield of 1,2,3-trichloro-*F*-propane based on injection of 1,2,3-trichloropropane was 69.8%. The ^{19}F NMR spectrum of 1,2-dichloro-*F*-adamantane showed peaks at −108.82, −112.22, −117.68, −121.16, −107.24, and −218.68 ppm (integral 1:4:4:2:1:2), the first four are in the CF_2 region and the last two are in the CF region. The tentative assignments are shown in

Table II. Parameters of Aerosol Fluorinations[a]

	fluorination					
	1	2	3	4	5	6
fluorine flow (mL/min)						
module 1-1	8	8	8	8	8	8
module 1-2	50	50	50	50	50	46
module 2-1	36	38	36	38	38	32
module 2-2	6	6	6	6	6	6
helium diluent (mL/min)						
module 1-1	170	170	170	170	170	170
module 1-2	170	170	170	170	170	170
module 2-1	170	170	170	170	170	170
module 2-2	170	170	170	170	170	170
main carrier (He, mL/min)	760	760	500	500	760	760
primary hydrocarbon carrier	135	135	48	48	55	135
secondary hydrocarbon carrier	825	825	552	552	825	840
reaction temp (°C)						
module 1	-10	-12	-10	-11	-10	-10
module 2	-6	-2	0	-1	0	-3
evaporator	142	142	102	102	142	107
injector	156	156	105	105	150	100
hydrocarbon throughput (mmol/h)	1.78	1.35	1.78	0.99	1.09	4.82
ratio (C-H:F_2)	1:3.2	1:3.4	1:4.6	1:4.7	1:3.5	1:3.4
isolated yield (%)	55.4	38.4	40.2	38.3	59.4	51.9

[a] Referring to aerosol fluorinator components described in ref 21.

Figure 2. The mass spectrum showed the following peaks: [*m/z* (formula, intensity)] 424 ($^{13}CC_9F_{14}{}^{37}Cl$, 6.0), 423 ($C_{10}F_{14}{}^{37}Cl$, 37), 422 ($^{13}CC_9F_{14}{}^{35}Cl$, 13), 421 ($C_{10}F_{14}{}^{35}Cl$, 100), 386 ($C_{10}F_{14}$, 7.5), and 367 ($C_{10}F_{13}$, 5.5). Anal. Calcd for $C_{10}F_{14}Cl_2$: C, 26.28; F, 58.20; Cl, 15.52. Found: C, 26.25; F, 57.90; Cl, 15.58. The vapor-phase infrared spectrum had absorption bands at 1290 (vs), 1272 (s), 1240 (vw), 1007 (w), 993 (vw), 974 (m), 956 (s), 877 (m), 850 (w), 832 (w), 809 (m), 668 (vw), and 651 (vw) cm^{-1}.

(3) Aerosol Fluorination of 1,3-Dichloroadamantane. 1,3-Dichloroadamantane (1.37 g, 6.68 mmol) was fluorinated as a solution in 1,1,2-trichloroethane (5.68 g, 42.5 mmol) over a period of 3.75 h. 1,3-Dichloro-*F*-adamantane (1.23 g, 2.69 mmol) was collected in the -22 °C trap and R-113 (3.6 g, 19.2 mmol) in the -78 °C trap. The percent yield of 1,3-dichloro-*F*-adamantane based on injection of 1,3-dichloroadamantane was 40.2% and the percent yield of R-113 based on injection of 1,1,2-trichloroethane was 45.2%. The ^{19}F NMR spectrum of 1,3-dichloro-*F*-adamantane consisted of four peaks at -107.19, -114.17, -120.80, and -215.68 ppm (integral 2:8:2:2); the assignments are shown in Figure 2. The mass spectrum showed the following prominent peaks: [*m/z* (formula, intensity)] 460 ($C_{10}F_{14}{}^{37}Cl_2$, 2.5), 458 ($C_{10}F_{14}{}^{37}Cl^{35}Cl$, 11), 456 ($C_{10}F_{14}{}^{35}Cl_2$, 17), 424 ($^{13}CC_9F_{14}{}^{37}Cl$, 4.0), 423 ($C_{10}F_{14}{}^{37}Cl$, 35), 422 ($^{13}CC_9F_{14}{}^{35}Cl$, 12), and 421 ($C_{10}F_{14}{}^{35}Cl$, 100). Anal. Calcd for $C_{10}F_{14}Cl_2$: C, 26.28; F, 58.20; Cl, 15.52. Found: C, 26.39; F, 58.10; Cl, 15.39. The vapor-phase infrared spectrum had absorption bands at 1289 (vs), 1274 (s), 1219 (vw), 1035 (w), 1030 (w), 1004 (m), 951 (s), 889 (m), 815 (w), 793 (m), and 649 (w) cm^{-1}.

(4) Aerosol Fluorination of 1,3,5-Trichloroadamantane. 1,3,5-Trichloroadamantane (1.07 g, 4.47 mmol) was fluorinated as a solution in 1,1,2-trichloroethane (6.32 g, 47.4 mmol) over a period of 3.5 h. 1,3,5-Trichloro-*F*-adamantane (0.86 g, 1.81 mmol) was collected in the -22 °C trap and R-113 (3.1 g, 16.5 mmol) in the -78 °C trap. The percent yield of 1,3,5-trichloro-*F*-adamantane based on injection of 1,3,5-trichloroadamantane was 38.3% and the percent yield of R-113 based on injection of 1,1,2-trichloroethane was 46.8%. The ^{19}F NMR spectrum of 1,3,5-trichloro-*F*-adamantane consisted of three peaks at -106.86, -113.77, and -213.00 ppm (integral 6:6:1); the first two are in the CF_2 region and the last is in the CF region. The unique bridgehead fluorine atom showed a clear heptet (J_{FF} = 13.67 Hz) and the ^{19}F NMR spectrum is consistent with its structure. The mass spectrum showed the following prominent peaks: [*m/z* (formula, intensity)] 478 ($C_{10}F_{13}{}^{37}Cl_3$, 1.0), 476 ($C_{10}F_{13}{}^{37}Cl_2{}^{35}Cl$, 3.7), 474 ($C_{10}F_{13}{}^{37}Cl^{35}Cl_2$, 12), 472 ($C_{10}F_{13}{}^{35}Cl_3$, 13), 441 ($C_{10}F_{13}{}^{37}Cl_2$, 15), 440 ($^{13}CC_9F_{13}{}^{37}Cl^{35}Cl$, 8), 439 ($C_{10}F_{13}{}^{37}Cl^{35}Cl$, 80), 438 ($^{13}CC_9F_{13}{}^{35}Cl_2$, 12), 437 ($C_{10}F_{13}{}^{35}Cl_2$, 100), 404 ($C_{10}F_{13}{}^{37}Cl$, 2.0), 402 ($C_{10}F_{13}{}^{35}Cl$, 5.0), and 367 ($C_{10}F_{13}$, 5.0). Anal. Calcd for $C_{10}F_{13}Cl_3$: C, 25.37; F, 52.17; Cl, 22.46. Found: C, 25.22; F, 52.04; Cl, 22.20. The vapor-phase infrared spectrum had absorption bands at 1278 (s), 1263 (vw), 1214 (w), 1178 (m), 1117 (m), 1044 (m), 999 (w), 914 (s), 816 (s), 794 (w), 718 (vw), and 655 (w) cm^{-1}.

(5) Aerosol Fluorination of 1,3,5,7-Tetrachloroadamantane. 1,3,5,7-Tetrachloroadamantane (1.49 g, 5.43 mmol) was fluorinated as a solution in 1,2,3-trichloropropane (9.53 g, 64.6 mmol) over a period of 5 h. Products were transferred to the vacuum line and worked up as described above. White solid (1.56 g) was collected in the -22 °C trap and 1,2,3-trichloro-*F*-propane (12.7 g, 53.4 mmol) in the -78 °C trap. The contents of the -22 °C trap were dissolved in $CFCl_3$ and separated on a Fluorosilicone QF-1 column (7 m × 3/8 in.) with the temperature program 170 °C, 10 min; 2 °C/min to 190 °C, 2 min; 5 °C/min to 210 °C. The products were identified as 1,3,5,7-tetrachloro-*F*-adamantane (t_R = 40.5 min) and 2-hydryl-1,3,5,7-tetrachloro-*F*-adamantane (t_R = 50 min) which constituted 61.3% and 38.7% of the total products collected by weight, respectively. The combined percent yield of these two products based on injection of 1,3,5,7-tetrachloroadamantane was 59.4% and the percent yield of 1,2,3-trichloro-*F*-propane based on injection of 1,2,3-trichloropropane was 82.7%. The ^{19}F NMR spectrum of 1,3,5,7-tetrachloro-*F*-adamantane had only one peak at -106.15 ppm, which is in the CF_2 region; there are no peaks in the CF region. The ^{13}C NMR spectrum consisted of a triplet at 112.2 ppm (J_{C-F} = 266.5 Hz) and a broad peak at 69.5 ppm. This is expected and is consistent with its structure since all bridgehead fluorine atoms are replaced by chlorine atoms. The mass spectrum showed the following prominent peaks: [*m/z* (formula, intensity)] 494 ($C_{10}F_{12}{}^{37}Cl_3{}^{35}Cl$, 3.0), 492 ($C_{10}F_{12}{}^{37}Cl_2{}^{35}Cl_2$, 12), 490 ($C_{10}F_{12}{}^{37}Cl^{35}Cl_3$, 25), 488 ($C_{10}F_{12}{}^{35}Cl_4$, 11), 457 ($C_{10}F_{12}{}^{37}Cl_2{}^{35}Cl$, 30), 455 ($C_{10}F_{12}{}^{37}Cl^{35}Cl_2$, 87), 453 ($C_{10}F_{12}{}^{35}Cl_3$, 100), 420 ($C_{10}F_{12}{}^{37}Cl^{35}Cl$, 2.0), and 418 ($C_{10}F_{12}{}^{35}Cl_2$, 28). Anal. Calcd for $C_{10}F_{12}Cl_4$: C, 24.52; F, 46.54; Cl, 28.94. Found: C, 24.45; F, 46.74; Cl, 29.21. The vapor-phase infrared spectrum had absorption bands at 1284 (sh), 1265 (vs), 1246 (sh), 1218 (s), 1132 (w), 1075 (w), 1025 (w), 976 (s), 789 (vs), 701 (vw), and 643 (s) cm^{-1}. The ^{19}F NMR spectrum of 2-hydryl-1,3,5,7-tetrachloro-*F*-adamantane gave three resonances at -105.22 (d, 4), -108.24 (d, 4, J_{FF} = 129.84 Hz), and -108.05 (s, 2, overlapped with one of above doublets) in the CF_2 region and one resonance at -208.11 (doublet of multiplet, 1) in the CFH region. The ^1H NMR spectrum gave one doublet at 4.79 ppm (J_{FH} = 43.57 Hz), which is similar with the ^1H NMR spectrum of 2-hydryl-*F*-adamantane.[13] The mass spectrum showed the following prominent peaks: [*m/z* (formula, intensity)] 440 ($C_{10}F_{11}{}^{37}Cl_3$, 8.0), 438 ($C_{10}F_{11}{}^{37}Cl_2{}^{35}Cl$, 26), 436 ($C_{10}F_{11}{}^{37}Cl^{35}Cl_2$, 100), 434 ($C_{10}F_{11}{}^{35}Cl_3$, 82), 417 ($C_{10}F_{10}{}^{37}Cl^{35}Cl_2$, 11), 403 ($C_{10}F_{11}{}^{37}Cl_2$, 8), 401 ($C_{10}F_{11}{}^{37}Cl^{35}Cl$, 37), and 399 ($C_{10}F_{11}{}^{35}Cl_2$, 56). Anal. Calcd for $C_{10}F_{11}Cl_4H$: C, 25.45; F, 44.28; Cl, 30.05; H, 0.21. Found: C, 25.66; F, 43.98; Cl, 29.85; H, 0.40. The vapor-phase infrared spectrum had absorption bands at 2965 (vw), 1265 (vs), 1238 (s), 1219 (s), 1212 (s), 1185 (w), 1162 (vw), 1143 (w), 1065 (w), 1042 (w), 977 (s), 971 (sh), 812 (m), 788 (vs), 700 (m), 662 (w), 644 (sh), 636 (m), 625 (m), and 584 (w) cm^{-1}.

(6) Aerosol Fluorination of 1-Chloronorbornane. 1-Chloronorbornane (2.84 g, 21.7 mmol) was fluorinated as a solution in 1,1,2-trichloroethane (3.87 g, 29.0 mmol) over a period of 4.5 h. 1-Chloro-*F*-norbornane (3.7 g, 11.2 mmol) was collected in the -22 °C trap and R-113 (4.7 g, 25.1 mmol) was collected in the -78 °C trap. The percent yield of 1-chloro-*F*-norbornane based on injection of 1-chloronorbornane was 51.9% and the percent yield of R-113 based on injection of 1,1,2-trichloroethane was 86.5%. The ^{19}F NMR spectrum of 1-chloro-*F*-norbornane consisted of two different overlapped AB spectra (ϕ_A = -112.80 ppm, ϕ_B = -122.74 ppm, J_{AB} = 247.01 Hz; $\phi_{A'}$ = -120.40 ppm, $\phi_{B'}$ = -125.36 ppm, $J_{A'B'}$ = 257.90 Hz), a singlet at -128.73 ppm in the CF_2 region, and a broad unresolved peak at -222.05 ppm in

the CF region. This is similar to ^{19}F NMR spectra of 1-hydryl- and 1-iodo-*F*-norbornanes.[24] The mass spectrum showed the following peaks: [*m/z* (formula, intensity)] 331 ($^{13}CC_6F_{11}{}^{37}Cl$, 2.5), 330 ($C_7F_{11}{}^{37}Cl$, 32), 329 ($^{13}CC_6F_{11}{}^{35}Cl$, 7.2), 328 ($C_7F_{11}{}^{35}Cl$, 100), 294 ($^{13}CC_6F_{11}$, 7.5), and 293 (C_7F_{11}, 93.5). Anal. Calcd for $C_7F_{11}Cl$: C, 25.59; F, 63.61; Cl, 10.79. Found: C, 25.36; F, 63.42; Cl, 10.62. The vapor-phase infrared spectrum had absorption bands at 1370 (m), 1303 (vs), 1276 (vs), 1251 (vs), 1201 (w), 1158 (w), 1083 (w) 1035 (sh), 1019 (s), 995 (m), 959 (s), 924 (s), 883 (s), 840 (m), 644 (m), 613 (s), 610 (sh), 524 (w), and 462 (w) cm^{-1}.

Reduction of Dichloro-*F*-adamantane Isomers. The mixture of 2,2-dichloro-*F*-adamantane, 2,4-dichloro-*F*-adamantane isomers (0.247 g, 0.54 mmol) and azobis(isobutyronitrile) (AIBN, 0.4 mg, as a radical initiator) were loaded into a Pyrex ampule covered with a rubber septum. The ampule was cooled to 0 °C, and *n*-Bu_3SnH (0.4 mL, 1.49 mmol) was injected by syringe under nitrogen. The reaction mixture was heated to 80 °C for 24 h followed by trap-to-trap vacuum line fractionation. The products (0.16 g, 0.41 mmol, 76%) were recovered as a white solid in the −22 °C trap. The white solid was dissolved in R-113 and separated on a Fluorosilicone QF-1 column with the temperature program 120 °C, 28 min; 20 °C/min to 160 °C. The isomers were identified as 2,2-dihydryl-*F*-adamantane (t_R = 21.9 min, 79.0%), 2,4-dihydryl-*F*-adamantane (3 isomers, t_R = 24.8 min, 13.7%), and possibly 2-hydryl-4-chloro-*F*-adamantane (isomers, t_R = 41.5 min, 7.3%). The ^{19}F NMR spectrum of 2,2-dihydryl-*F*-adamantane consisted of four unresolved peaks at −122.28, −124.35, −205.68, and −224.00 ppm (integral 2:8:2:2); the first two are in the CF_2 region and the last two are in the CF region which is similar to that of 2,2-dichloro-*F*-adamantane. Its ^1H NMR spectrum had a peak at 2.67 ppm. The mass spectrum showed the following peaks: [*m/z* (formula, intensity)] 386 ($C_{10}F_{14}$, 1.5), 374 (C_9F_{14}, 1.0), 369 ($^{13}CC_9F_{13}H$, 12), 368 ($C_{10}F_{13}H$, 100), and 348 ($C_{10}F_{12}$, 13). Anal. Calcd for $C_{10}F_{14}H_2$: C, 30.94; F, 68.53; H, 0.52. Found: C, 31.05; F, 68.71; H, 0.71. The vapor-phase infrared spectrum had absorption bands at 2949 (vw), 1349 (w), 1297 (vs), 1267 (s), 1240 (w), 1152 (s), 1116 (m), 1008 (vs), 981 (s), 935 (s), 931 (sh), and 883 (w) cm^{-1}. The ^{19}F NMR spectrum of 2,4-dihydryl-*F*-adamantane (3 isomers) had peaks at −120.68, −123.37, −204.71, −213.78, −215.17, −220.75, −224.25, and −225.41 ppm. Their ^1H NMR spectrum had an expected doublet of multiplets at 5.18 ppm (J_{HF} = 47.50 Hz). The tentative assignments of both ^{19}F NMR spectra are showed in Figure 4. The mass spectrum showed the following peaks: [*m/z* (formula, intensity)] 369 ($^{13}CC_9F_{13}H$, 11.5), 368 ($C_{10}F_{13}H$, 100), and 348 ($C_{10}F_{12}$, 14.2). Anal. Calcd for $C_{10}F_{14}H_2$: C, 30.94; F, 68.53; H, 0.52. Found: C, 30.79; F, 68.75; H, 0.80. The vapor-phase infrared spectrum had absorption bands at 2997 (vw), 1353 (w), 1307 (s), 1290 (vs), 1275 (vs), 1222 (w), 1159 (w), 1109 (m), 1017 (m), 979 (s), 956 (s), 915 (s), and 860 (w) cm^{-1}.

(24) Mooney, E. F. *An Introduction to ^{19}F NMR Spectroscopy*; Heyden & Son Ltd.: London, 1970; p 35.