J. Org. Chem. 1994, 59, 1115-1118 1115

Photochemical Reduction of *F*-Adamantyl Halides: A Facile Synthesis of Hydrylfluorocarbons from Chlorofluorocarbons

James L. Adcock* and Huimin Luo

Department of Chemistry, University of Tennnessee, Knoxville, Tennessee 37996-1600

Received July 27, 1993•

1-Chloro- and 2-chloro-*F*-adamantanes, 1,2- and 1,3-dichloro-*F*-adamantanes, 1,3,5-trichloro-*F*-adamantane, 1,3,5,7-tetrachloro-*F*-adamantane, 1-bromo-*F*-adamantane, and 1-iodo-*F*-adamantane dissolved in $CFCl_3$ are conveniently dehalogenated in the presence of methanol, hexane, or other hydrogen donor cosolvents by ultraviolet irradiation. The reactions are very clean with isolated yields in the range of 80%-90%. Generally, irradiation times increase when large batches of material are photolyzed and when the less reactive secondary *F*-adamantyl chlorides are reduced. By controlling the irradiation time, polychloro-*F*-adamantanes can be reduced in a stepwise manner. Only free-radical, not ionic, products are isolated. A possible mechanism for this photochemical reduction is discussed.

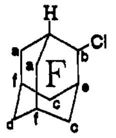
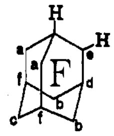
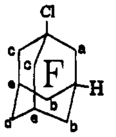
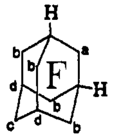
Introduction

Recently, we reported the syntheses of several useful *F*-adamantyl chlorides[1] and polychlorides.[2] Although the most synthetically useful monovalent substituent groups on perfluorocarbons are the iodides and bromides,[3] the perfluoroalkyl bromides are less reactive and are rarely used if the iodides are available. However, neither of these substituents will survive attack by elemental fluorine as can the chlorides.[4] Although less reactive than the bromides and the iodides, *F*-adamantyl chlorides can be converted into hydryl-*F*-adamantanes,[1] which readily undergo metalation with halide-free methyllithium. If necessary, addition of iodine or bromine readily produces *F*-adamantyl iodides or bromides.[5] The method previously used to convert 1-chloro- and 2-chloro-*F*-adamantanes into hydryl-*F*-adamantanes required tributyltin hydride, an expensive reagent. Herein, we report an inexpensive photochemical reduction method which can convert polychloro-*F*-adamantanes stepwise into chlorohydryl-*F*-adamantanes, eventually producing hydryl-*F*-adamantanes in good yields. The advantages of this method are cost and control; the reaction progress can be easily monitored by changes in the ^{19}F NMR spectra and controlled by irradiation time. Paleta and co-workers at the Prague Institute of Chemical Technology have done work in this area, but their compounds usually contained a carboxylic acid group next to the halogen substituent.[6,7]

Results

Irradiation of 1-chloro-*F*-adamantane for 5 h in a $CFCl_3$ solution containing a stoichiometric excess of methanol afforded 1-hydryl-*F*-adamantane in 86.6% yield. Irradiation of 1-bromo-*F*-adamantane for 30 min and irradiation of 1-iodo-*F*-adamantane for 15 min conducted as outlined above also afforded 1-hydryl-*F*-adamantane in high yields which in each case was identified by comparison with an authentic sample.[1] Irradiation of 2-chloro-*F*-adamantane for 10 h conducted as outlined above afforded 2-hydryl-*F*-adamantane in 81% yield and was also identified by comparison with an authentic sample.

Table 1. ^{19}F NMR Chemical Shifts (ppm) of 1,2- and 1,3-Disubstituted *F*-Adamantanes

	$\phi_a = -106.75$ $\phi_b = -113.63$ $\phi_c = -117.10$ $\phi_d = -120.79$ $\phi_e = -208.58$ $\phi_f = -218.43$		$\phi_a = -107.85$ $\phi_b = -110.69$ $\phi_c = -119.35$ $\phi_d = -210.75$ $\phi_e = -215.67$ $\phi_f = -219.66$
	$\phi_a = -101.61$ $\phi_b = -108.67$ $\phi_c = -113.70$ $\phi_d = -120.43$ $\phi_e = -217.20$		$\phi_a = -95.09$ $\phi_b = -108.24$ $\phi_c = -120.40$ $\phi_d = -221.00$

1-Hydryl-2-chloro-*F*-adamantane in 50.7% GC yield was identified by ^{19}F NMR after 20 min UV irradiation of 1,2-dichloro-*F*-adamantane (77 mg). Pure 1,2-dihydryl-*F*-adamantane was isolated after 112 h UV irradiation of 1,2-dichloro-*F*-adamantane (380 mg). The tentative assignments and ^{19}F NMR spectra of new 1,2-disubstituted *F*-adamantanes are listed in Table 1. The spectral pattern of 1-hydryl-2-chloro-*F*-adamantane is similar to that of 1,2-dichloro-*F*-adamantane while that of 1,2-dihydryl-*F*-adamantane is different from that of 1,2-dichloro-*F*-adamantane. Complete characterizations of all new compounds are given in the Experimental Section.

1-Chloro-3-hydryl-*F*-adamantane was formed after 15 min UV irradiation of 1,3-dichloro-*F*-adamantane (94 mg). 1,3-Dihydryl-*F*-adamantane was isolated after 70 h UV irradiation of 1,3-dichloro-*F*-adamantane (337 mg). The tentative assignments and ^{19}F NMR spectra of new 1,3-disubstituted *F*-adamantanes are listed in Table 1.

1,3-Dichloro-5-hydryl-*F*-adamantane was formed in 53.5% GC yield after UV irradiation of 1,3,5-trichloro-*F*-adamantane (101 mg) for only 5 min. 1-Chloro-3,5-dihydryl-*F*-adamantane was formed in 56.1% GC yield after 2 h UV irradiation of 1,3,5-trichloro-*F*-adamantane (95 mg). 1,3,5-Trihydryl-*F*-adamantane was isolated in 86.4% yield after 70 h UV irradiation of 1,3,5-trichloro-*F*-adamantane (400 mg). The tentative assignments and ^{19}F NMR spectra of new 1,3,5-trisubstituted *F*-adaman-

---

• Abstract published in *Advance ACS Abstracts*, February 15, 1994.

[1] Adcock, J. L.; Luo, H.; Zuberi, S. S. *J. Org. Chem.* **1992**, *57*, 4749.

[2] Adcock, J. L.; Luo, H. *J. Org. Chem.* **1993**, *58*, 1704.

[3] Banks, R. E. *Fluorocarbons and Their Derivatives*, 2nd ed.; Macdonald: London, 1970; pp 79, 102.

[4] Adcock, J. L.; Cherry, M. L. *Ind. Eng. Chem. Res.* **1987**, *26*, 208.

[5] Luo, H. Ph.D. Dissertation, The University of Tennessee at Knoxville, Dec 1992.

[6] Shendrik, V. P.; Paleta, O.; Dedek, V. *Collect. Czech. Chem. Commun.* **1976**, *41*, 874.

[7] Paleta, O. *J. Fluorine Chem.* **1991**, *54*, 97.

0022-3263/94/1959-1115$04.50/0

Table 2. ^{19}F NMR Chemical Shifts (ppm) of 1,3,5-Trisubstituted *F*-Adamantanes

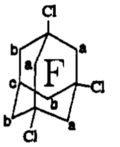
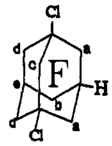
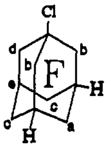
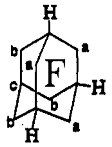
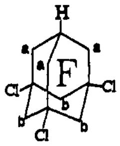
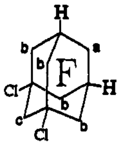
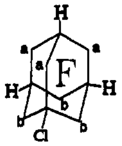
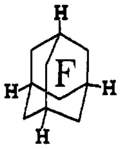
	$\phi_a = -106.86$ $\phi_b = -113.77$ $\phi_c = -213.00$		$\phi_a = -100.99$ $\phi_b = -106.24$ $\phi_c = -108.02$ $\phi_d = -113.19$ $\phi_e = -215.67$
	$\phi_a = -94.62$ $\phi_b = -100.70$ $\phi_c = -107.84$ $\phi_d = -113.70$ $\phi_e = -220.81$		$\phi_a = -94.04$ $\phi_b = -107.44$ $\phi_c = -227.08$

Table 3. ^{19}F NMR Chemical Shifts (ppm) of 1,3,5,7-Tetrasubstituted *F*-Adamantanes

	$\phi_a = -101.01$ $\phi_b = -106.18$		$\phi_a = -94.56$ $\phi_b = -100.61$ $\phi_c = -106.22$
	$\phi_a = -94.09$ $\phi_b = -100.21$		$\phi_a = -93.33$

tanes are listed in Table 2. 1,3,5-Trichloro-7-hydryl-*F*-adamantane was formed after 15 min UV irradiation of 1,3,5,7-tetrachloro-*F*-adamantane (88 mg) in methanol. After an additional 75 min irradiation, 1,3-dichloro-5,7-dihydryl-*F*-adamantane was formed. 1-Chloro-3,5,7-trihydryl-*F*-adamantane was formed after an additional 200 min UV irradiation. 1,3,5,7-Tetrahydryl-*F*-adamantane was formed after 16 h UV irradiation of 1,3,5,7-tetrachloro-*F*-adamantane. Its ^{19}F NMR spectrum had a single peak at −93.33 ppm. The tentative assignments and ^{19}F NMR Spectra of new 1,3,5,7-tetrasubstituted *F*-adamantanes are listed in Table 3.

As can be seen from Tables 1–3, the chemical shifts of the fluorine β to the substituent moved to lower field upon replacement of a chlorine atom with a hydrogen atom. This shift is in contradiction to that predicted by the inductive effects and indicates that the inductive effect is much less important in perfluorocarbon compounds than through bond paramagnetic shielding effects.[8]

Discussion

The photochemistry of nonfluorinated alkyl bromides and iodides has been extensively studied by Kropp and co-workers.[9–11] Generally, irradiation of alkyl halides in solution affords complicated product mixtures.[12] In contrast to these results, our UV irradiation of the six chloro-*F*-adamantanes, 1-bromo-*F*-adamantane, and 1-iodo-*F*-adamantane give only the corresponding free-radical products (hydryl-*F*-adamantanes) in the presence of methanol, hexane, or other hydrogen donor solvents containing about 50% $CFCl_3$. The reactions are very clean, and the isolated yields were in the range of 80%–90%. The absence of *any* side reaction is clearly due to the strong, nonpolarizable C–F bond which provides the carbon backbone with excellent protection from chemical attack. Generally, irradiation times increase when large batches of material are photolyzed and when the less reactive secondary *F*-adamantyl chlorides are reduced (vida infra). By controlling the irradiation time, polychloro-*F*-adamantanes can be reduced stepwise. This absence of competing reactions provides an easy and inexpensive method for the synthesis of hydryl-*F*-adamantanes, which can be easily derivatized.

Table 4. Ultraviolet Absorption Band Maxima and Their Molar Extinction Coefficients[a]

compds	λ_{max} (nm)	ϵ_{max} (L·mol^{-1}·cm^{-1})
1-iodo-*F*-adamantane	224	1011
1-bromo-*F*-adamantane	220	632
1-chloro-*F*-adamantane	216	174
2-chloro-*F*-adamantane	215	95
1,2-dichloro-*F*-adamantane	216	209
1,3-dichloro-*F*-adamantane	218	203
1,3,5-trichloro-*F*-adamantane	218	229
1,3,5,7-tetrachloro-*F*-adamantane	216	354

[a] Solvent used for measuring UV spectra is diethyl ether.

It is generally accepted that the photochemical reactions of alkyl halides are induced by the lowest energy transition (n → σ^*), which involves the excitation of a nonbonding electron of the halogen (X) atom to the antibonding molecular orbital (σ^* MO) of the C–X bond. It also is observed that the absorption band is "red-shifted" (the so-called "bathochromic shift") as the atomic number of the halogen (X) increases and that the absorption band increases in intensity as the number of halogen atoms increases.[13] Our experimental UV spectral data shown in Table 4 clearly reflect these assertions, thus: $\lambda_{max}(X = I) > \lambda_{max}(X = Br) > \lambda_{max}(X = Cl)$ and $\epsilon_{max}(X = I) > \epsilon_{max}(X = Br) > \epsilon_{max}(X = Cl)$ for the halo-*F*-adamantanes. This is virtually the same phenomenon found for nonfluorinated alkyl halides. The fact that borosilicate glassware was employed in all our photochemical reactions precludes any photochemical reaction mechanism involving a direct n → σ^* excitation of our *F*-adamantyl halides since virtually all of these compounds have neglegible absorption at wavelengths above 280 nm, the region through which borosilicate glassware transmits light. Clearly, the addition of $CFCl_3$ to our photolysis solutions is important. This has prompted us to propose a radical abstraction mechanism induced by the absorption of photons by $CFCl_3$, as shown in Scheme 1. This proposition is based on the fact that the irradiations were conducted in a solvent mixture that was 50% $CFCl_3$. $CFCl_3$ exhibits a complex absorption centered about 220 nm, a strong shoulder at 196 nm, a weak shoulder at 240 nm, and tails to wavelengths beyond 350 nm. A $CFCl_3$-mediated photoreduction mechanism is supported by the fact that $CFCl_3$ undergoes to a small (ca. 10%) degree a simultaneous reaction resulting in formation of $CFCl_2H$ and $CFCl_2CFCl_2$ (10:1) and the observation that the adamantyl dehalogenation reaction is much slower in the absence of $CFCl_3$. Any other role that $CFCl_3$ may play as a sensitizer or energy transfer agent to the *F*-adamantyl halides is unclear. Consistent with the proposed photochemically induced halogen abstraction mechanism is the observation that the rate of

---

(8) Adcock, J. L.; Luo, H.; Dai, S. *Magn. Reson. Chem.* **1993**, *31*, 969–971.

(9) Kropp, P. J. *Acc. Chem. Res.* **1984**, *17*, 131.

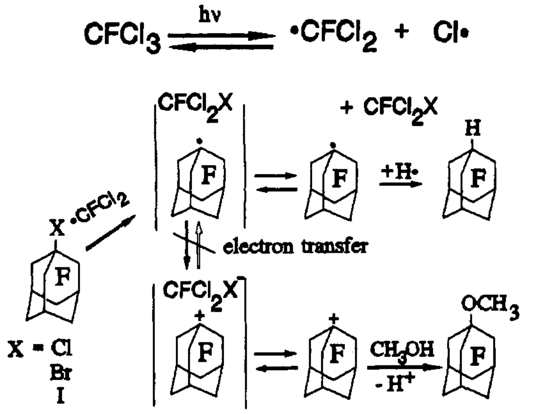
(10) Kropp, P. J.; Sawyer, J. A.; Snyder, J. J. *J. Org. Chem.* **1984**, *49*, 1583.

(11) Kropp, P. J.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. *J. Am. Chem. Soc.* **1976**, *98*, 8135.

(12) For a review of the photobehavior of alkyl halides in solution, see: Lodder, G. In *The Chemistry of Functional Groups, Supplement D;* Patai, S., Rappoport, Z., Eds.; Wiley: London, 1983; Chapter 29.

(13) Kopecky, J. *Organic Photochemistry: A Visual Approach;* VCH Publisher: New York, 1992; p 184.

Scheme 1



the photochemical reduction follows the order 1-iodo-*F*-adamantane > 1-bromo-*F*-adamantane > 1-chloro-*F*-adamantane, a rate order inversely proportional to the C–X bond energy. Since the rate of radical abstraction by $CFCl_2^{\cdot}$ should depend on the C–X bond strength, a rate order of C–I > C–Br > C–Cl >> C–F is expected. Since the C–F bond (bond energy: 116 kcal/mol) is the strongest known single bond to carbon, it is not surprising that $CFCl_2^{\cdot}$ cannot abstract $F^{\cdot}$ from *F*-adamantanes to produce byproducts. This undoubtedly is the principal reason the photochemical reduction of *F*-adamantyl chlorides has synthetic value. The C–H bond (bond energy: 98 kcal/mol) is not as strong as a C–F bond; thus, the photogenerated radical $CFCl_2^{\cdot}$ should more readily abstract an $H^{\cdot}$ from a nonfluorinated adamantane giving rise to potentially many byproducts. Consequently, the photochemical reactions of nonfluorinated adamantyl chlorides will not likely be found to have synthetic utility.[14]

In conclusion, chlorine atoms on the *F*-adamantyl skeleton can be replaced with hydrogen atoms in a stepwise manner using a simple photochemical reduction. This provides an inexpensive method for the synthesis of many desirable mixed hydryl/chloro-*F*-adamantanes or completely dechlorinated hydryl-*F*-adamantanes. Unlike nonfluorinated alkyl chlorides where photochemical reactions have almost no synthetic value, photochemical reduction of perfluoroadamantyl chlorides in methanol/$CFCl_3$ provides an efficient method for the preparation of perfluoroadamantyl hydrides which are good synthons for the synthesis of other perfluoroadamantyl derivatives or perfluoroadamantyl-substituted organic compounds.

Experimental Section

General. 1-Chloro- and 2-chloro-*F*-adamantane, 1,2- and 1,3-dichloro-*F*-adamantane, 1,3,5-trichloro-*F*-adamantane, and 1,3,5,7-tetrachloro-*F*-adamantane syntheses are described in previous work.[1,2] The products were manipulated on a vacuum line; some purifications could be achieved by fractionation using slush baths, but where needed gas chromatography was used for purification [Bendix Model 2300 with subambient multicontroller and 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)]. 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. The products were characterized by vapor-phase infrared spectra recorded on a Bio-Rad Spc 3200 spectrometer. Negative chemical ionization (electron attachment) mass spectra were recorded on a VG.ZAB-EQ mass spectrometer. Samples were introduced into the source via the reference inlet to a pressure of 10^{-6} Torr and diluted with nitrogen gas to 10^{-5} to 10^{-4} Torr and bombarded with 70-eV electrons. ^{19}F NMR spectra were determined on a JEOL FX90Q FTNMR spectrometer (using the omniprobe and NM-PVTS1 programmable VT system) in $CFCl_3$ as both solvent and internal standard. UV spectra were recorded on a HP 8452 diode array spectrophotometer, HP89530 MS-DOS UV/vis. Elemental analyses were performed by E+R Microanalytical Lab., Inc., Corona, NY.

Irradiation. Irradiations were carried out using a 550-W medium-pressure mercury lamp (Ace-Hanovia) in a water-cooled quartz immersion well. During irradiation, the enclosure's atmospheric temperature increased to about 120 °C. During irradiation about 10% of the $CFCl_3$ is converted (10:1) to $CFCl_2H$ [$\phi_F = -80.79$ ppm (d), $\delta_H = 7.39$ ppm (d), $J_{HF} = 58.2$ Hz] and $CFCl_2CFCl_2$ [$\phi_F = -67.71$ ppm (s)] suggesting that it plays an energy conversion role in the experiments which tend to proceed slower in its absence.

Monitoring ^{19}F NMR Experiments. In a typical small-scale reaction, 50–100 mg of the substrate was dissolved in an excess amount of methanol (0.3 g) containing 0.3–0.5 g of $CFCl_3$ (since methanol is not a good solvent for these perfluorinated compounds) and was syringed into a 5-mm borosilicate NMR tube. The NMR tube was evacuated and sealed on a vacuum line, placed near the water-cooled immersion well, and irradiated. ^{19}F NMR spectra were recorded every 5 min at the beginning of the irradiation and then every 10, 20, 30 min, and 1 h when longer irradiation times were needed. After irradiation, the NMR tube was connected to the vacuum line. The products were isolated by trap to trap fractionation and GC purified wherever necessary.

Preparative-Scale Irradiations. In a typical run, 0.3–0.4 g of the substrate was dissolved in an excess amount of methanol (1.0–1.5 g) containing 1.0–1.5 g of $CFCl_3$ and was syringed into a 100-mL borosilicate bulb equipped with a Teflon stopcock and glass joint to connect the bulb to the vacuum line. The reactants were degassed and irradiated. After irradiation, the bulb was connected to the vacuum line. The products were isolated by trap to trap fractionation followed by GC purification where ever needed.

Irradiation of 1-Chloro-*F*-adamantane. Small-scale irradiation of 1-chloro-*F*-adamantane (56.6 mg, 0.128 mmol) for 5 h conducted as outlined above afforded 1-hydryl-*F*-adamantane (45 mg, 0.110 mmol, 86.6%) which was identified by comparison with an authentic sample.

Irradiation of 2-Chloro-*F*-adamantane. Small-scale irradiation of 2-chloro-*F*-adamantane (67.1 mg, 0.152 mmol) for 10 h conducted as outlined above afforded 2-hydryl-*F*-adamantane (50 mg, 0.125 mmol, 81%) which was identified by comparison with an authentic sample.

Irradiation of 1,2-Dichloro-*F*-adamantane. Small-scale irradiation of 1,2-dichloro-*F*-adamantane (77 mg, 0.168 mmol) for 20 min conducted as outlined above afforded 1-hydryl-2-chloro-*F*-adamantane (36 mg, 0.085 mmol, 50.7% GC yield). Its ^{19}F NMR spectrum had peaks at −106.75, −113.63, −117.10, −120.79, −208.58, and −218.43 (int 4:1:4:2:1:2); the first four are in the CF_2 region, and the last two are in the CF region. The ^1H NMR spectrum of 1-hydryl-2-chloro-*F*-adamantane had a multiplet at 3.95 ppm. Prominent peaks in the mass spectrum of 1-hydryl-2-chloro-*F*-adamantane were [*m*/*z* (formula, int)] 423 ($C_{10}F_{14}{}^{37}Cl$, 2.0), 421 ($C_{10}F_{14}{}^{35}Cl$, 3.5), 404 ($C_{10}F_{13}{}^{37}Cl$, 2.0), 402 ($C_{10}F_{13}{}^{35}Cl$, 4.0), 387 ($^{13}CC_9F_{14}$, 11), and 386 ($C_{10}F_{14}$, 100). The vapor-phase infrared spectrum showed bands at 2941 (w), 1323 (s), 1292 (vs), 1288 (s), 1260 (s), 1212 (w), 1132 (m), 1096 (w), 993 (s), 956 (m), 935 (s), 870 (m), 735 (w), 667 (w) cm^{-1}. Anal. Calcd for $C_{10}F_{14}ClH$: C, 28.42; F, 62.95; Cl, 8.39; H, 0.24. Found: C, 28.54; F, 62.72; Cl, 8.09; H, 0.26.

Preparative-scale irradiation of 1,2-dichloro-*F*-adamantane (0.38 g, 0.831 mmol) for 70 h conducted as outlined above afforded 0.35 g of white solid which was composed of 1,2-dihydryl-*F*-adamantane and 1-hydryl-2-chloro-*F*-adamantane (72:28). Further irradiation of this mixture for an additional 42 h produced pure 1,2-dihydryl-*F*-adamantane (0.28 g, 0.7216 mmol, 86.7%). Its ^{19}F NMR spectrum had peaks at −107.47 (d), −108.23 (d), −110.69, −119.35, −121.19, and −123.26 ppm in the CF_2 region and three multiplets at −210.75, −215.67, −219.66 ppm (int 1:1:2) in

---

(14) Gilbert, A.; Baggott, J. *Essentials of Molecular Photochemistry*; CRC Press: Boca Raton, FL, 1991; p 466.

the CHF and CF region. The ^1H NMR spectrum consisted of two peaks at 3.78 ppm (m) and 5.35 ppm (d of m). The prominent peaks in the mass spectrum of 1,2-dihydryl-*F*-adamantane were [*m/z* (formula, int)] 388 ($C_{10}F_{14}H_2$, 17.5), 387 ($C_{10}F_{14}H$, 5.0), 369 ($^{13}CC_9F_{13}H$ and $C_{10}F_{13}H_2$, 32.5), 368 ($C_{10}F_{13}H$, 100), and 348 ($C_{10}F_{12}$, 16). The vapor-phase infrared spectrum showed bands at 2950 (w), 2913 (w), 1323 (m), 1296 (s), 1269 (s), 1236 (m), 1144 (m), 998 (s), 971 (m), 952 (s), 933 (m), 847 (vw), 737 (vw) cm^{-1}. Anal. Calcd for $C_{10}F_{14}H_2$: C, 30.94; F, 68.53; H, 0.52. Found: C, 31.06; F, 68.63; H, 0.75.

Irradiation of 1,3-Dichloro-*F*-adamantane. Small-scale irradiation of 1,3-dichloro-*F*-adamantane (94.8 mg, 0.207 mmol) for 15 min conducted as outlined above afforded 1-chloro-3-hydryl-*F*-adamantane (46 mg, 0.108 mmol, 52.1% GC yield). Its ^{19}F NMR spectrum consisted of four peaks at −101.61, −108.67, −113.70, and −120.43 in the CF_2 region and one peak at −217.20 ppm in the CF region (int 2:4:4:2:2). The ^1H NMR spectrum showed a peak at 3.53 ppm. The prominent peaks in the mass spectrum of 1-chloro-3-hydryl-*F*-adamantane were [*m/z* (formula, int)] 424 ($C_{10}F_{14}{}^{37}ClH$, 9.8), 422 ($C_{10}F_{14}{}^{35}ClH$, 28.5), 404 ($C_{10}F_{13}{}^{37}Cl$, 2.5), 402 ($C_{10}F_{13}{}^{35}Cl$, 7.5), 388 ($^{13}CC_9F_{14}H$, 6.0), 387 ($C_{10}F_{14}H$, 54), 386 ($C_{10}F_{14}$, 39), 369 ($^{13}CC_9F_{13}H$, 9.5), 368 ($C_{10}F_{13}H$, 100), and 348 ($C_{10}F_{12}$, 14). The vapor-phase infrared spectrum showed bands at 2934 (w), 1327(vs), 1290 (s), 1257 (s), 1237 (w), 1138 (s), 1124 (w), 996 (s), 961 (w), 930 (m), 856 (m), 733 (w), 601 (w) cm^{-1}. Anal. Calcd for $C_{10}F_{14}ClH$: C, 28.42; F, 62.95; Cl, 8.39; H, 0.24. Found: C, 28.70; F, 62.94; Cl, 8.14; H, 0.45.

Preparative-scale irradiation of 1,3-dichloro-*F*-adamantane (0.337 g, 0.7374 mmol) for 70 h conducted as outlined above gave 1,3-dihydryl-*F*-adamantane (0.25 g, 0.6443 mmol, 87.4%). Its ^{19}F NMR spectrum had peaks at −95.09, −108.24, −120.40, and −221.00 ppm (int 2:8:2:2), the first three being in the CF_2 region and the last one in the CF region. The ^1H NMR spectrum of 1,3-dihydryl-*F*-adamantane had a peak at 3.75 ppm. The prominent peaks in the mass spectrum of 1,3-dihydryl-*F*-adamantane were [*m/z* (formula, int)] 388 ($C_{10}F_{14}H_2$, 8.0), 387 ($C_{10}F_{14}H$, 63), 386 ($C_{10}F_{14}$, 46), 369 ($^{13}CC_9F_{13}H$, 10), 368 ($C_{10}F_{13}H$, 100), 367 ($C_{10}F_{13}$, 5.6), and 348 ($C_{10}F_{12}$, 20). The vapor-phase infrared spectrum showed bands at 2943 (w), 2891 (w), 1138 (vs), 1310 (vs), 1284 (m), 1268 (m), 1236 (m), 1165 (m), 1138 (m), 1086 (m), 914 (m), 766 (w), 649 (w), 512 (w) cm^{-1}. Anal. Calcd for $C_{10}F_{14}H_2$: C, 30.94; F, 68.53; H, 0.52. Found: C, 30.80; F, 68.20; H, 0.63.

Irradiation of 1,3,5-Trichloro-*F*-adamantane. Small-scale irradiation of 1,3,5-trichloro-*F*-adamantane (101.3 mg, 0.214 mmol) for 5 min conducted as outlined above afforded 1,3-dichloro-5-hydryl-*F*-adamantane (50.3 mg, 0.114 mmol, 53.5% GC yield). Its ^{19}F NMR spectrum had peaks at −100.99, −106.24, −108.02, −113.19, and −215.67 ppm (int 4:2:2:4:1); the first four are in the CF_2 region, and the last one is in the CF region. The ^1H NMR spectrum showed a peak at 3.52 ppm. The prominent peaks in the mass spectrum of 1,3-dichloro-5-hydryl-*F*-adamantane were [*m/z* (formula, int)] 442 ($C_{10}F_{13}{}^{37}Cl_2$, 5.0), 440 ($C_{10}F_{13}{}^{37}Cl^{35}Cl$, 55), 438 ($C_{10}F_{13}{}^{35}Cl_2$, 97), 405 ($^{13}CC_9F_{13}{}^{37}Cl$ and $C_{10}F_{13}H^{37}Cl$, 35), 404 ($^{13}CC_9F_{13}H^{35}Cl$ and $C_{10}F_{13}{}^{37}Cl$, 75), 403 $^{13}CC_9F_{13}{}^{35}Cl$ and $C_{10}F_{13}H^{35}Cl$, 82), 402 ($C_{10}F_{13}{}^{35}Cl$, 100), 385 ($C_{10}F_{12}{}^{37}Cl$, 4.5), and 383 ($C_{10}F_{12}{}^{35}Cl$, 11). The vapor-phase infrared spectrum showed bands at 2927 (w), 1329 (s), 1313 (s), 1292 (vs), 1283 (s), 1254 (s), 1148 (w), 1123 (w), 1086 (w), 987 (m), 963 (w), 891 (m), 817 (w), 794 (w), 584 (w), 481 (m) cm^{-1}. Anal. Calcd for $C_{10}F_{13}Cl_2H$: C, 27.36; F, 56.26; Cl, 16.15; H, 0.23. Found: C, 27.40; F, 56.08; Cl, 16.44; H, 0.34.

Small-scale irradiation of 1,3,5-trichloro-*F*-adamantane (95.2 mg, 0.201 mmol) for 2 h conducted as outlined above afforded 1-chloro-3,5-dihydryl-*F*-adamantane (49.5 mg, 0.113 mmol, 56.1% GC yield). Its ^{19}F NMR spectrum had peaks at −94.62, −100.70, −107.84, −113.70, and −220.81 ppm (int 2:4:4:2:1), the first four being in the CF_2 region and the last in the CF region. The ^1H NMR spectrum showed a peak at 3.42 ppm. The prominent peaks in the mass spectrum of 1-chloro-3,5-dihydryl-*F*-adamantane were [*m/z* (formula, int)] 407 ($^{13}CC_9F_{13}{}^{37}ClH_2$, 4.0), 406 ($C_{10}F_{13}{}^{37}ClH_2$, 38), 405 ($^{13}CC_9F_{13}{}^{35}ClH_2$, 12), 404 ($C_{10}F_{13}{}^{35}ClH_2$, 100), 386 ($C_{10}F_{12}{}^{37}ClH$, 3.5), 384 ($C_{10}F_{12}{}^{35}ClH$, 9.0), 369 ($C_{10}F_{13}H_2$ or $^{13}CC_9F_{13}H$, 9.5), 368 ($C_{10}F_{13}H$, 67), 366 ($C_{10}F_{11}{}^{37}Cl$, 4.0), and 364 ($C_{10}F_{11}{}^{35}Cl$, 10). The vapor-phase infrared spectrum showed bands at 2925 (w), 1333 (vs), 1295 (s), 1255 (s), 1244 (m), 1162 (m), 1143 (m), 1112 (m), 1086 (m), 983 (s), 864 (m), 620 (w), 510 (w) cm^{-1}; HR mass calcd for $C_{10}F_{13}ClH_2$ 403.9637, found 403.9641.

Preparative-scale irradiation of 1,3,5-trichloro-*F*-adamantane (0.4 g, 0.844 mmol) for 70 h conducted as outlined above gave 1,3,5-trihydryl-*F*-adamantane (0.27 g, 0.73 mmol, 86.4%). Its ^{19}F NMR spectrum had peaks at −94.04, −107.44, and −227.08 ppm (int 6:6:1); the first two are in the CF_2 region, and the last one is in the CF region. The ^1H NMR spectrum of 1,3,5-trihydryl-*F*-adamantane had a peak at 3.62 ppm. The prominent peaks in the mass spectrum of 1,3,5-trihydryl-*F*-adamantane were [*m/z* (formula, int)] 370 ($C_{10}F_{13}H_3$, 1.0), 369 ($C_{10}F_{13}H_2$, 12), 368 ($C_{10}F_{13}H$, 51), 351 ($^{13}CC_9F_{12}H_2$, 9.0), 350 ($C_{10}F_{12}H_2$, 100), 331 ($C_{10}F_{11}H_2$, 5.3), and 330 ($C_{10}F_{11}H$, 38). The vapor-phase infrared spectrum showed bands at 2921 (w), 1344 (vs), 1312 (vs), 1263 (m), 1234 (w), 1163 (sh), 1151 (s), 1136 (w), 1084 (m), 981 (s), 796 (w), 667 (w), 508 (w) cm^{-1}. Anal. Calcd for $C_{10}F_{13}H_3$: C, 32.45; F, 66.73; H, 0.82. Found: C, 32.67; F, 66.54; H, 0.71.

Irradiation of 1,3,5,7-Tetrachloro-*F*-adamantane. Small-scale irradiation of 1,3,5,7-tetrachloro-*F*-adamantane (88 mg, 0.18 mmol) for 15 min, conducted as outlined above, afforded 1,3,5-trichloro-7-hydryl-*F*-adamantane which was identified by ^{19}F NMR spectroscopy. Its ^{19}F NMR spectrum had peaks at −101.01 and −106.18 ppm (int 1:1), which are in the CF_2 region. After an additional 75 min irradiation, 1,3-dichloro-5,7-dihydryl-*F*-adamantane was observed by ^{19}F NMR spectroscopy. Its ^{19}F NMR spectrum had peaks at −94.56, −100.61, and −106.22 ppm (int 2:8:2), which are in the CF_2 region. 1-Chloro-3,5,7-trihydryl-*F*-adamantane was formed after an additional 200 min irradiation. Its ^{19}F NMR spectrum had peaks at −94.09 and −100.21 ppm (int 1:1), which are in the CF_2 region. 1,3,5,7-Tetrahydryl-*F*-adamantane which had a peak at −93.33 ppm was identified after 16 h UV irradiation of 1,3,5,7-tetrachloro-*F*-adamantane.

Irradiation of 1-Bromo-*F*-adamantane. Small-scale irradiation of 1-bromo-*F*-adamantane (38.6 mg, 0.0796 mmol) for 30 min conducted as outlined above afforded 1-hydryl-*F*-adamantane which was identified by comparison with an authentic sample.

Irradiation of 1-Iodo-*F*-adamantane. Small-scale irradiation of 1-iodo-*F*-adamantane (30.3 mg, 0.0569 mmol) for 15 min conducted as outlined above afforded 1-hydryl-*F*-adamantane which was identified by comparison with an authentic sample.

Acknowledgment. One of the authors (HL) would like to acknowledge Professors Richard R. Pagni and Ronald M. Magid of this department for helpful discussions. Graduate student support of the University of Tennessee Science Alliance is also gratefully acknowledged.