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Syntheses and Photochemical Reactions of Perfluorinated Carbonyl-Containing Adamantane Derivatives

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F-4-Oxahomoadamantan-5-one, *F*-4-protoadamantanone, and *F*-adamantane-2,4-dione have been synthesized for the first time by aerosol direct fluorination of their corresponding hydrocarbons. UV irradiation of *F*-4-oxahomoadamantan-5-one produces *F*-oxaadamantane, the corresponding decarbonylation product: its first reported synthesis. UV irradiation of *F*-4-protoadamantanone gave *F*-noradamantane, the same product as from UV irradiation of *F*-adamantanone. All new products were characterized by mass spectrometry, ^{19}F NMR, FT-IR spectroscopy, and elemental analysis.

Introduction

Adamantane has interested chemists for nearly a century and research based on its unusual chemical and physical properties has led to important advances in several areas of organic chemistry.[2,3] Many adamantane derivatives such as adamantanone[4] have been synthesized. Some adamantane derivatives have even found applications in medicine.[5] However, fewer fluorinated adamantane derivatives are known. Our interest is to fill this gap. We have been interested in preparing new perfluorodiamondoid compounds for several years and have reported successful syntheses of *F*-adamantane,[6] *F*-diamantane,[7] and numerous chloro-*F*-adamantanes[8,9] by aerosol direct fluorination, all 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 an 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 perfluorination takes place. Product aerosols are collected in a 2–3 in. bed of sodium fluoride pellets cooled by N_2(l). This predominantly free radical process has been previously applied to the synthesis of perfluorinated carbonyl-containing compounds.[10,11] The aerosol direct fluorination of adamantanone produced the perfluorinated analogue in good yield with no decarbonylated product.[12] This encouraged us to look more extensively into the aerosol direct fluorination of other carbonyl-containing adamantane derivatives as a means by which preselected survivable sites for subsequent reaction could be incorporated into the organic molecules prior to their fluorination. In this paper, we wish to report aerosol fluorination of 4-oxahomoadamantan-5-one (**1**), 4-protoadamantanone (**2**), and adamantane-2,4-dione (**3**). Photochemical reactions of *F*-4-oxahomoadamantan-5-one (**4**) and *F*-4-protoadamantanone (**5**) are also discussed.

Results and Discussion

With the help of spectroscopic techniques (vide infra), the virtually pure products (excluding cofluorinating solvents) directly collected from the reactor following aerosol direct fluorination of **1**, **2**, and **3** were identified in each case as the corresponding perfluorinated compound with no decarbonylated products. However the yields of **4**, **5**, and **6** isolated, based on the amounts injected, are only 30.7%, 23.5%, and 22.4%, respectively, due to losses inherrent in the collection/recovery process. Direct fluorination of cage hydrocarbons into their perfluorinated analogues with little carbon framework rearrangement or fragmentation has been achieved by other techniques;[13] however, little additional work has been published. The sensitivity of many functionalized cage compounds to the HF generated during fluorination is a problem in nonaerosol fluorinations, one of which has been partly addressed.[14] In the aerosol process possible photolysis of the carbonyl group during photochemical finishing of the fluorination was a concern.[15] The successful syntheses of **4**, **5**, and **6** further suggest that photolysis of perfluorinated ketones or lactones occurs too slowly to be important on the reactor time scale of about 1 min.

Unlike *F*-adamantanone, which is not hygroscopic and does not dissolve in or react with water to any detectible extent, pure *F*-adamantane-2,4-dione (**6**) rapidly picks up moisture while dissolved in $CFCl_3$. The ^{19}F NMR spectrum of (**6**) has three well-separated singlets in the CF region at −207.85, −216.36, and −224.65 ppm (integral 1:2:1), although it gives unresolved complicated peaks in the CF_2 region. ^{19}F NMR spectra indicated that

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[2] Fort, R. C.; Schleyer, P. v. R. *Chem. Rev.* **1964**, *64*, 277.

[3] Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 3189.

[4] Schleyer, P. v. R.; Nicholas, R. D. *J. Am. Chem. Soc.* **1961**, *83*, 182.

[5] Wishnok, J. S. *J. Chem. Educ.* **1973**, *50*, 780.

[6] Adcock, J. L.; Robin, M. L. *J. Org. Chem.* **1983**, *48*, 3128.

[7] Adcock, J. L.; Luo, H. *J. Org. Chem.* **1992**, *57*, 2162.

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

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

[10] Adcock, J. L.; Robin, M. L. *J. Org. Chem.* **1983**, *48*, 2437.

[11] Adcock, J. L.; Robin, M. L. *J. Org. Chem.* **1984**, *49*, 1442.

[12] Adcock, J. L.; Luo, H. *J. Org. Chem.* **1992**, *57*, 4297.

[13] Robertson, G.; Liu, E. K. S.; Lagow, R. J. *J. Org. Chem.* **1978**, *43*, 4981.

[14] Bierschenk, T. R.; Juhlke, T. J.; Lagow, R. J. U.S. Patent No. 4 755 567, 1988.

[15] Giacometti, G.; Okabe, H.; Price, S. J. Steacie, E. W. R. *Can. J. Chem.* **1960**, *38*, 104.

0022-3263/94/1959-5883$04.50/0

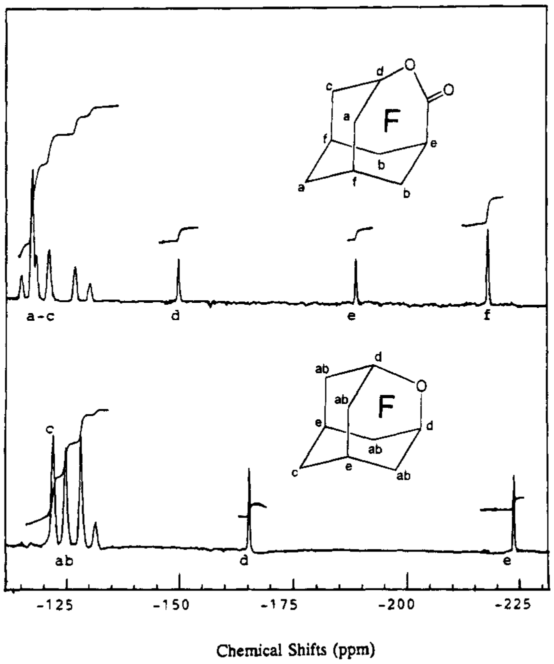


Figure 1.

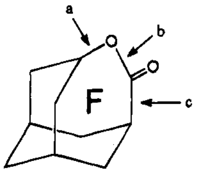
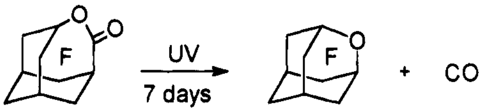


Figure 2.

the signals corresponding to **6** decreased gradually while new peaks at −141.43, −178.75, and −201.95 ppm, which may be assigned to the hydrate and dihydrate of **6**, appear gradually while sitting at room temperature. The addition of the second carbonyl group to the adamantanone framework significantly alters the chemical behavior. The most intense peak in the mass spectrum of **6** is the molecular ion minus COF_2, and interestingly, the second strongest peak is due to loss of a second COF_2.

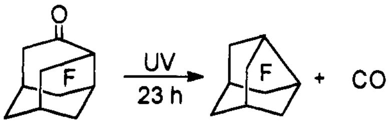
UV irradiation of *F*-4-oxahomoadamantan-5-one (**4**) in $CFCl_3$ solution resulted in the formation of *F*-2-oxaadamantane (**7**). This reaction can be easily monitored by ^{19}F NMR because the two compounds have very different ^{19}F NMR spectra (see Figure 1). As with the hydrocarbon lactones,[16] UV irradiation of **4** hypothetically can result in the initial breakage of any one of three different bonds (labeled a, b, and c in Figure 2) which lead to product. Although the presently available data are insufficient for a mechanistic interpretation, the fact that **7** was isolated in 84% yield from this solution photolysis with no detectible *F*-noradamantane (the decarboxylation product) clearly favors bond breakage at b and/or c over bond breakage at a. The reaction therefore takes place by extrusion of CO (not CO_2) followed by radical recombination to form a C−O bond (eq 1). This result is consistent with UV irradiation of another fluorinated lactone.[17] The photochemical extrusion of CO from the perfluorinated lactone is in sharp contrast with the photodecarboxylation of the nonfluorinated lactone.[18]



(1)

The ^{19}F NMR spectrum of **7** exhibits an AB pattern ($\phi_A = -123.57$, $\phi_B = -129.21$ ppm, $J_{AB} = 274.02$ Hz) overlapped with a singlet at −121.96 ppm in the CF_2 region and two unresolved peaks at −165.25 and −223.71 ppm in the CF region. The infrared spectrum proved the absence of a C=O group in agreement with the expected chemical structure of this compound.

UV irradiation of *F*-4-protoadamantanone (**5**) in $CFCl_3$ solution produced *F*-noradamantane, an identical product to that generated in the photochemical reaction of *F*-adamantanone.[11] A mechanism similar to that for *F*-adamantanone, i.e., extrusion of CO followed by radical recombination to form a C−C bond, is indicated by eq 2.



(2)

The fact that the same photochemical product is formed from these two different precursors reinforces the CO extrusion mechanism. The reason for the much longer reaction time required for photochemical decarbonylation of *F*-4-oxahomoadamantan-5-one (**4**) than for either *F*-adamantanone or *F*-4-protoadamantanone (**5**) is not clear. The UV cut-off of the borosilicate glass NMR tubes is about 280 nm. Although a blue shift of the $n \rightarrow \pi^*$ transition energy (216 to 214 nm), which results from the interaction between the nonbonding electrons of the saturated oxygen and the π orbitals of the carbonyl group, thus raising the energy of the π^* orbital, may play a role. Thus the $n \rightarrow \pi^*$ transition in the (perfluorinated) lactone would require appreciably more energy than in the ketones.[19] The fact that borosilicate glassware was employed in all our photochemical reactions precludes any photochemical reaction mechanism involving a direct $n \rightarrow \pi^*$ excitation of our *F*-adamantanones (216 to 214 nm). However, virtually all of these compounds have weak absorptions (ca. 10% of $n \rightarrow \pi^*$ maximum) at wavelengths above 280 nm, the region through which borosilicate glassware transmits light. Clearly, photochemical pumping of these lower bands might induce the decarbonylation. The use of $CFCl_3$ as solvent for our photolysis may also be important. $CFCl_3$ exhibits a complex absorption centered about 220 nm, a strong shoulder at 196 nm, and a weak shoulder at 240 nm, which tails to wavelengths beyond 350 nm. This has prompted us to consider the possibility of an energy-transfer mechanism involving the absorption of photons by $CFCl_3$. A $CFCl_3$-mediated photochemical decarbonylation mechanism is supported circumstantially by the observance of a $CFCl_3$-mediated photochemical reduction of *F*-adamantyl halides.[20]

Experimental Section

The perfluorinations were carried out on an improved reactor; detailed operating procedures have been described elsewhere.[21] The detailed fluorination conditions for each

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[16] Simonaitis, R.; Pitts, J. N., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 1389.

[17] Throckmorton, J. R. *J. Org. Chem.* **1969**, *34*, 3438.

[18] Coyle, J. D. *Chem. Rev.* **1978**, *78*, 97.

[19] Gibert, A.; Baggott, J. *Essentials of Molecular Photochemistry*; Blackwell: London, 1991; p 328.

[20] Adcock, J. L.; Luo, H. *J. Org. Chem.* **1994**, *59*, 1115.

Table 1. Parameters of Aerosol Fluorinations[a]

	1	**2**	**3**
fluorine flow (mL/min)			
module 1-1[a]	8	8	8
module 1-2[a]	52	50	52
module 2-1[a]	38	36	38
module 2-2[a]	6	6	6
[a]helium diluent (mL/min each)	170	170	170
main carrier (He, mL/min)	760	760	760
primary hydrocarbon carrier	135	135	135
secondary hydrocarbon carrier	820	820	820
reaction temperatures (°C)			
module 1	−10	−10	−12
module 2	−3	0	0
evaporator	140	141	138
injector	150	156	155
hydrocarbon throughput (mmol/h)	0.909	1.98	1.44
ratio (H_2:F_2)	1:5.79	1:3.75	1:4.02
product	**4**	**5**	**6**
product yield (%)	30.7	23.5	22.4

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

compound are listed in Table 1. 4-Oxahomoadamantan-5-one,[22] 4-protoadamantanone,[23] and adamantane-2,4-dione were synthesized and purified by literature procedures. The fluorinated products were characterized by vapor phase infrared spectra recorded on a Bio-Rad Spc 3200 spectrometer. The negative chemical ionization (electron attachment) mass spectrum was 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. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY. Photolyses were carried out using a 550 W medium-pressure mercury lamp (Ace-Hanovia), in a water-cooled quartz immersion well.

Aerosol Direct Fluorination of 4-Oxahomoadamantan-5-one (1). A solution of **1** (0.835 g; 5.00 mmol) in 1,2,3-trichloropropane (5.59 g; 37.9 mmol) was fluorinated over a period of 5.5 h. Virtually pure *F*-4-oxahomoadamantan-5-one (**4**) (0.653 g; 1.54 mmol) was collected in the −22 °C trap and 1,2,3-trichloro-*F*-propane (5.34 g; 22.5 mmol) in the −78 °C trap. The yield of **4** based on injection of **1** was 30.7%; the yield of 1,2,3-trichloro-*F*-propane based on injection of 1,2,3-trichloropropane was 59.3%. The ^{19}F NMR spectrum of **4** consisted of a plethora of peaks from −114.71 to −129.96 ppm in the CF_2 region and three peaks at −149.61, −188.56, and −217.88 ppm (integral 1:1:2) in the CF region. This is consistent with its structure. The mass spectrum showed the following peaks [*m/z* (formula, rel intensity)]: 391 ($^{13}CC_8F_{14}O$, 8.0); 390 ($C_9F_{14}O$, 100); 375 ($^{13}CC_8F_{14}$, 2.0); 374 (C_9F_{14}, 14). Anal. Calcd for $C_{10}F_{14}O_2$: C, 28.73; F, 63.62. Found: C, 28.61; F, 63.46. The vapor phase infrared spectrum had absorption bands at 1844 (m), 1285 (vs), 1253 (sh), 1174 (vw), 1152 (vs), 1129 (sh), 1072 (w), 1029 (w), 1005 (w), 976 (vs), 938 (w) cm^{-1}.

Aerosol Direct Fluorination of 4-Protoadamantanone (2). A solution of **2** (1.34 g; 8.92 mmol) in 1,2,3-trichloropropane (5.78 g; 39.2 mmol) was fluorinated over a period of 4.5 h. Virtually pure *F*-4-protoadamantanone (**5**) (0.845 g; 2.10 mmol) was collected in the −22 °C trap and 1,2,3-trichloro-*F*-propane (7.70 g; 32.4 mmol) in the −78 °C trap. The yield of **5** based on injection of **2** was 23.5%; 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 **5** consisted of a plethora of peaks from −112.76 to −125.47 ppm in the CF_2 region and three peaks at −196.27, −213.43, and −222.19 ppm (integral 1:2:1) in the CF region. The mass spectrum showed the following peaks [*m/z* (formula, rel intensity)]: 403 ($^{13}CC_9F_{14}O$, 6.0); 402 ($C_{10}F_{14}O$, 60.5); 374 (C_9F_{14}, 11.5); 364 ($C_{10}F_{12}O$, 35.8); 355 (C_9F_{13}, 8.5); 337 ($^{13}CC_8F_{12}$, 8.8); 336 (C_9F_{12}, 100). Anal. Calcd for $C_{10}F_{14}O$: C, 29.87; F, 66.15. Found: C, 30.16; F, 65.92. The vapor phase infrared spectrum had absorption bands at 1808 (m), 1350 (sh), 1315 (s), 1292 (s), 1273 (vs), 1252 (s), 1225 (m), 1190 (vw), 1046 (w), 1006 (w), 972 (vs), 951 (s), and 916 (s) cm^{-1}.

Aerosol Direct Fluorination of Adamantane-2,4-dione (3). A solution of **3** (0.826 g; 5.04 mmol) in 1,2,3-trichloropropane (4.88 g; 33.1 mmol) was fluorinated over a period of 3.5 h. Virtually pure *F*-adamantane-2,4-dione (**6**) (0.43 g; 1.13 mmol) was collected in the −22 °C trap and 1,2,3-trichloro-F-propane (6.2 g; 26.1 mmol) in the −78 °C trap. The yield of **6** based on injection of **3** was 22.4%; the yield of 1,2,3-trichloro-*F*-propane based on injection of 1,2,3-trichloropropane was 78.7%. The ^{19}F NMR spectrum of **6** consisted of a plethora of peaks from −116.74 to −133.43 ppm in the CF_2 region and three peaks at −207.85, −216.36, and −224.65 ppm (integral 1:2:1) in the CF region. This is consistent with its structure. The mass spectrum showed the following peaks [*m/z* (formula, rel intensity)]: 380 ($C_{10}F_{12}O_2$, 1.0); 352 ($C_9F_{12}O$, 0.5); 315 ($^{13}CC_8F_{10}O$, 8.0); 314 ($C_9F_{10}O$, 100); 276 (C_9F_8O, 10.3); and 248 (C_8F_8, 23.4). The vapor phase infrared spectrum had absorption bands at 1824 (w), 1799 (m), 1286 (s), 1267 (s), 1236 (w), 1029 (m), 977 (s), 962 (m), and 950 (w) cm^{-1}.

Photolysis of *F*-4-Oxahomoadamantan-5-one (4). A solution of **4** (0.0758 g, 0.181 mmol) in 0.647 g of $CFCl_3$ (R-11) contained in a 5 mm borosilicate NMR tube was sealed on a vacuum line and then irradiated by the mercury lamp for 7 days. During irradiation, the atmospheric temperature was increased to about 120 °C. After irradiation, the NMR tube was reconnected to the vacuum line. Following trap to trap fractionation, *F*-2-oxadamantane (**7**) (0.060 g, 0.153 mmol, 84.8%) was obtained as a white solid in the −22 °C trap. Gas chromatographic separation on a Fluorosilicone QF-1 column (7 m × $^3/_8$ in.) showed only one peak. The ^{19}F NMR spectrum of **7** consisted of an AB pattern ($\phi_A = -123.57$ ppm, $\phi_B = -129.21$ ppm, $J_{AB} = 274.01$ Hz) and a singlet at −121.96 ppm in the CF_2 region and two unresolved peaks at −165.25 and −223.71 ppm in the CF region. The mass spectrum showed the following peaks [*m/z* (formula, rel intensity)]: 391 ($^{13}CC_8F_{14}O$, 8.0); 390 ($C_9F_{14}O$, 100); 371 ($C_9F_{13}O$, 1.5); 324 (C_8F_{12}, 8.0). Anal. Calcd for $C_9F_{14}O$: C, 27.71; Found: C, 27.48. The vapor phase infrared spectrum had absorption bands at 1315 (s), 1287 (vs), 1276 (sh), 1188 (vw), 1123 (vs), 1078 (w), 1045 (w), 986 (m), 969 (s), 945 (m), 912 (w) cm^{-1}.

Photolysis of *F*-4-Protoadamantanone (5). A solution of **5** (0.026 g, 0.0646 mmol) in 0.526 g of $CFCl_3$ (R-11) contained in a 5 mm borosilicate NMR tube was sealed on a vacuum line and then irradiated by the mercury lamp for 22 h. During irradiation, the atmospheric temperature was increased to about 120 °C. ^{19}F NMR showed that **5** was converted quantitatively into *F*-noradamantane.

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(21) Adcock, J. L.; Cherry, M. L. *Ind. Eng. Chem. Res.* **1987**, *26*, 208.

(22) Faulkner, D.; McKervey, M. A. *J. Chem. Soc. C* **1971**, 3906.

(23) Majerski, Z.; Hamersak, Z. *Org. Synth.* **1979**, *59*, 147.