

## Communications to the Editor

### New Reaction of Saturated Fluorocarbons: Partial Reduction by NH<sub>3</sub> with Hg Photosensitization

Juan Burdeniuc, William Chupka, and Robert H. Crabtree\*

Department of Chemistry, Yale University  
225 Prospect Street, New Haven, Connecticut 06511

Received June 26, 1995

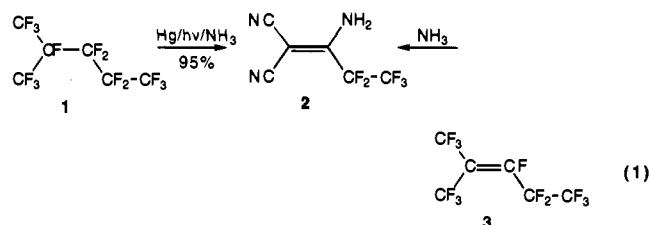
Saturated fluorocarbons are among the most inert chemical compounds and reactions involving them are extremely rare.<sup>1,2</sup> Their exceptional stability gives them important industrial applications<sup>3</sup> and makes the discovery of new conversion reactions a challenge for synthetic chemists. The chemistry of fluorocarbons has recently received increased attention, in part owing to the growing concern over the impact of chlorofluorocarbons (CFCs) on the upper atmosphere.<sup>4</sup> Reactions with strong reducing agents such as alkali or alkaline earth metals are very difficult to control and lead to complete defluorination;<sup>5a</sup> indeed, such reactions are used in quantitative analysis of perfluoroalkanes.<sup>5b</sup> MacNicol and Robertson<sup>5c</sup> have reported an electron transfer reaction in which sodium benzenethiolate slowly reacts with perfluorocarbons having tertiary carbon centers, leading to complete defluorination and aromatization to give C<sub>10</sub>(SPh)<sub>8</sub>. Recently, d- and f-block metal species, such as (MeC<sub>5</sub>H<sub>4</sub>)<sub>3</sub>U(Bu),<sup>6</sup> CpFe(CO)<sub>2</sub>,<sup>7a</sup> and Cp<sub>2</sub>Co,<sup>7b</sup> have been shown to be capable of defluorinating perfluoroalkanes, in one case<sup>7b</sup> to give free perfluoroarene. Catalytic CF reduction in the more reactive perfluoroarenes has also been reported recently,<sup>7c</sup> and stoichiometric CF activation in perfluoroarenes and -alkenes is much more common<sup>7d</sup> than that in perfluoroalkanes.

Functionalized perfluoroalkyl derivatives are of intense technological interest,<sup>8</sup> and therefore, ways to make them from the readily available perfluoroalkanes would be valuable. Stopping at the partial reduction stage is difficult because the partially reduced species tend to be more reactive than the

starting materials. In a significant advance, Pez and co-workers<sup>9</sup> have shown how a judicious choice of radical anion as reductant allows cyclic saturated perfluoroalkanes to be selectively converted into perfluoroarenes. We now report a controllable functionalization of perfluoroalkanes to give perfluoroalkyl derivatives via a new reaction.

We have previously reported a method for the partial oxidation of alkanes using vapor phase Hg photosensitization.<sup>10</sup> Under our conditions, this reaction shows essentially complete selectivity for volatile materials: when an alkane is functionalized and so becomes much less volatile, it condenses and is protected from further conversion. It did not seem obvious how this system, which relies on radical abstraction, could be adapted for reaction with perfluoroalkanes, which are inert to attack by radicals, but we nevertheless looked at a number of variants. We were very pleased to find that Hg photosensitization of a variety of perfluoroalkanes in the presence of NH<sub>3</sub> does, indeed, lead to partial reduction to give a single major product.

Purified<sup>11a</sup> (CF<sub>3</sub>)<sub>2</sub>CFCF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub> (**1**, 3 g, 8.9 mmol) was irradiated at 40 °C in a quartz tube for 19 h with 254 nm light from a *low-pressure* Hg lamp (Rayonet RMR-600, 32 W), with a drop of Hg (0.1 g) and with a flow of NH<sub>3</sub> gas (2 mL/min) (eq 1).<sup>10</sup> The experimental details are the same as those



described for non-fluorocarbon applications of these NH<sub>3</sub> reactions.<sup>10d</sup> The major products were NH<sub>4</sub>F and compound **2**, formed in good chemical (95%) and quantum yield (0.02) and isolated by chromatography on silica with CH<sub>2</sub>Cl<sub>2</sub>/THF (95:5 v/v) as eluent.<sup>11b</sup> Being involatile under the reaction conditions, **2** is protected from overreduction. Compound **2** was identified by comparison with literature data [mp 201–202 °C, lit.<sup>11c</sup> mp 201–203 °C; UV (EtOH) λ 287 nm (ε = 12 500), lit.<sup>11c</sup> λ 287 nm (ε = 13 750)]. In addition, **2** has a mass of 211 Da by GC-MS and shows a fragmentation pattern consistent with the

(9) Marsella, J. A.; Gilicinski, A. G.; Coughlin, A. M.; Pez, G. P. *J. Org. Chem.* **1992**, *57*, 2856.

(10) (a) Michos, D.; Sassano, D. A.; Krajnik, P.; Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1491. (b) Krajnik, P.; Michos, D.; Crabtree, R. H. *New J. Chem.* **1993**, *17*, 805. (c) Krajnik, P.; Crabtree, R. H. *Inorg. Chem.* **1993**, *32*, 1028. (d) Krajnik, P.; Crabtree, R. H. *New J. Chem.* **1993**, *17*, 559.

(11) (a) Commercial **1** (TCL) contained traces of unsaturated fluorocarbons which were eliminated by reaction with *n*-BuNH<sub>2</sub>. After filtration of the fluorimines and *n*-BuNH<sub>3</sub>F, the material was washed with 1.0 M HCl and then with water. **1** was then dried over MgSO<sub>4</sub> and distilled (fraction collected, 59–61 °C). The UV spectra of all starting materials showed that unsaturated perfluoroalkanes were completely absent. (b) Quantum yields relative to Et<sub>3</sub>SiH (Φ = 0.8). (c) Josey, A. D. *J. Org. Chem.* **1964**, *29*, 707. (d) Olivier, J. A.; Stephens, R.; Tatlow, J. C.; Taylor, J. R. *J. Fluorine Chem.* **1976**, *7*, 555. (e) Phull, G. S.; Plevy, R. G.; Tatlow, J. C. *J. Chem. Soc., Perkin Trans. 1* **1984**, 455. (f) <sup>1</sup>H NMR (CH<sub>2</sub>Cl<sub>2</sub>-d<sub>2</sub>): δ 1.56 (s, 2H); 2.12 (s, 1H); 5.5 (br, 1H). <sup>19</sup>F NMR (CH<sub>2</sub>Cl<sub>2</sub>-d<sub>2</sub>): δ -78.18 (m, J<sub>FF</sub> = 18.0 Hz, 3F); -111.3 (dt, J<sub>FF</sub> = 290.0 Hz, J<sub>FF</sub> = 15.20 Hz, 1F); -122.12 (m, J<sub>FF</sub> = 290 Hz, J<sub>FF</sub> = 12.2 Hz, 1F); -127.25 (dt, J<sub>FF</sub> = 272 Hz, J<sub>FF</sub> = 17.7 Hz, 1F); -139.0 (dm, J<sub>FF</sub> = 272 Hz, J<sub>FF</sub> = 12.2 Hz, 1F). MS (70 eV): *m/e* 275 (M<sup>+</sup>), 274 (M<sup>+</sup> - H), 247 (M<sup>+</sup> - H - CN), 244 (M<sup>+</sup> - H - 2HN), 254 (M<sup>+</sup> - H - HF), 177 (M<sup>+</sup> - H - HF - CF<sub>2</sub>CNH), 69 (CF<sub>3</sub>), 100 (C<sub>2</sub>F<sub>4</sub>). IR (NaCl film): ν 3410 (NH), 2919 (CH), 2215 (nitrile), 1647 (C=C), 1604 (NH), 1190 (CF), 1327 (CF). U.V (CH<sub>2</sub>Cl<sub>2</sub>): λ 218 (ε = 2800), 254 (ε = 1900), 265 (ε = 2500).

(1) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 341.

(2) Smart, B. E. In *The Chemistry of Halides, Pseudo-Halides and Azides*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; Suppl. D, pp 604–606.

(3) (a) Anderson, R. F.; Punderson, J. O. In *Organofluorine Chemicals and Their Industrial Applications*; Banks, R. E., Ed.; Ellis Horwood: Chichester, 1979; pp 235–247. (b) Slinn, D. S. L.; Green, S. W. In *Preparation, Properties and Industrial Applications of Organofluorine Compounds*; Banks, R. E., Ed.; Ellis Horwood: Chichester, 1982; pp 45–82. (c) Chambers, R. D. *Fluorine in Organic Chemistry*; Wiley: New York, 1973; pp 3–4.

(4) Ravishankara, A. R.; Solomon, S.; Turnipseed, A. A.; Warren, R. F. *Science* **1993**, *259*, 194.

(5) (a) Sheppard, W. A.; Sharts, C. M. *Organic Fluorine Chemistry*; W. A. Benjamin: New York, 1969; p 450. (b) Hudlicky, M. *Chemistry of Organic Fluorine Compounds*; Ellis Horwood: Chichester, 1976; pp 563–566. (c) Perry, R. *Fluorine—The First Hundred Years*; Banks, R. E., Sharp, D. W. A., Tatlow, J. C., Eds.; Elsevier: New York, 1986; pp 293–295. (d) MacNicol, D. D.; Robertson, C. D. *Nature* **1988**, *332*, 59.

(6) Weydert, M.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 8837.

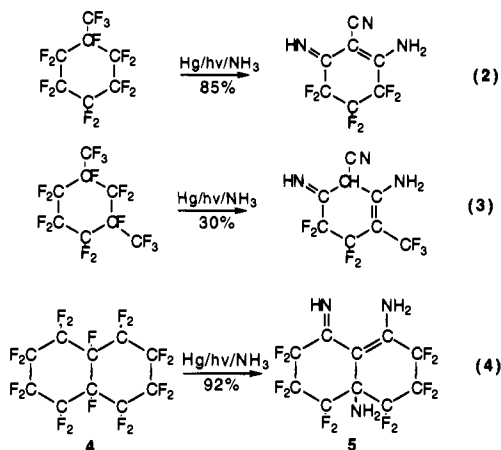
(7) (a) Harrison, R. G.; Richmond, T. G. *J. Am. Chem. Soc.* **1993**, *115*, 5303. (b) Bennett, B. K.; Harrison, R. G.; Richmond, T. G. *J. Am. Chem. Soc.* **1994**, *116*, 11165. (c) Aizenberg, M.; Milstein, D. *Science* **1994**, *265*, 359. (d) For example: Richmond, T. G. *Coord. Chem. Rev.* **1990**, *105*, 221. Belt, S. T.; Helliwell, M.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 1429. Blum, O.; Frolow, D.; Milstein, D. *J. Chem. Soc., Chem Commun.* **1991**, 258. Burk, M. J.; Staley, D. L.; Tumas, W. J. *Chem. Soc., Chem Commun.* **1990**, 809. Watson, P. L.; Tulip, T. H.; Williams, I. *Organometallics* **1990**, *9*, 1999.

(8) Hudlicky, M. *Chemistry of Organic Fluorine Compounds*; Pergamon Press: Oxford, 1961; pp 355–357.

proposed structure, notably the presence of strong peaks at  $m/e = 185$  and  $142$ , corresponding to loss of CN and  $CF_3$ , respectively. The  $C_2F_5$  group resonated in the  $^{19}F$  NMR spectrum at  $-80.7$  and  $-115.3$  ppm. The IR spectrum showed the CN groups ( $\nu(CN) = 2207\text{ cm}^{-1}$ ) and the  $NH_2$  group ( $\nu(NH_2) = 3312, 3181\text{ cm}^{-1}$ ).

We find that a plausible intermediate in the process, the alkene **3**, reacts with  $NH_3$  (1 atm, room temperature) to give the same dinitrile **2**, probably via a known<sup>12</sup> series of nucleophilic addition reactions of  $NH_3$ , followed by loss of HF and readdition of  $NH_3$ .

Other perfluoroalkanes having tertiary CF bonds react similarly, as shown in eqs 2–4. For the products of eqs 2 and



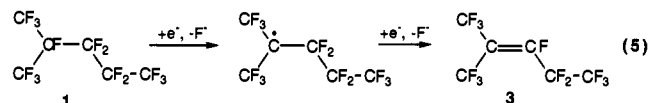
**4**, the compounds were identified by comparison with literature data.<sup>11d,e</sup> The product from eq 3 is a new compound, identified from its characteristic spectroscopic and mass spectral data.<sup>11f</sup>

We were puzzled as to how initial attack could take place on the perfluoroalkanes, since they are usually inert to radical attack, and Hg photosensitization is known<sup>13</sup> to proceed by radical formation. In particular, Hg photosensitization of  $NH_3$  is believed to give H atoms and  $NH_2$  radicals. Since the HF bond strength is higher, but the N–F bond strength is lower than the C–F bond strength, only H atoms could possibly abstract F from perfluoroalkanes. We therefore looked at the

Hg-photosensitized reaction of perfluorodecalin (**4**) in the presence of  $H_2$ , where H atoms are known to be the exclusive radicals formed. This gave no significant HF formation, confirming that H atoms are *not* the reactive species. Excited state Hg ( $Hg^*$ ) itself can be excluded, since it failed to attack **4** in the absence of  $NH_3$ . Finally, a control reaction in which Hg was omitted gave no reaction.

Many prior perfluorocarbon reactions<sup>5,7a-c,9</sup> are thought to proceed via initial electron transfer. The rate of reaction for **4**  $\rightarrow$  **5** proved to depend on  $[P(NH_3)]^2$  in the range 0.1–1 atm, and there was no H/D isotope effect ( $k_H/k_D = 1.0 \pm 0.1$ ). A possible mechanism, therefore, is electron transfer from an exciplex<sup>14</sup> such as  $[Hg^*(NH_3)_2]$ , but other pathways cannot be excluded. Such an exciplex should be a significant electron donor; indeed, the calculated vertical IP (3.72 eV)<sup>15a</sup> is very low and comparable to that of Cs (3.89 eV).<sup>15b</sup>

Once initial electron transfer has taken place, the sequence of eq 5 becomes possible, based on proposed<sup>16</sup> electron transfer



chemistry of perfluoroalkyl polymers. Loss of HF is no doubt assisted by the  $NH_3$  medium. Once **3** is formed, conversion to **2** can occur via dark reactions (eq 1).

The reaction is also effective for the surface modification of poly(tetrafluoroethylene) (PTFE). We exposed a strip of PTFE to ammonia in a quartz tube containing a drop of mercury, irradiated (254 nm) for 72 h, and measured the water contact angle in the product. The starting strip had a contact angle with water of  $108^\circ$ , indicating a very hydrophobic surface, but after treatment, the polymer had a contact angle of  $50^\circ$ , indicating that the surface had become much less hydrophobic. IR study of the modified PTFE film showed a weak band in the range  $1630\text{--}1700\text{ cm}^{-1}$  that we assign to  $\nu(C=NH)$ , suggesting that imine groups are present on the modified surface. This implies that secondary CF bonds, such as those present in PTFE, do react slowly under our conditions.

**Acknowledgment.** We thank Prof. P. E. M. Siegbahn (Stockholm) for providing an unpublished result and 3M Corp. for funding.

JA952096G

(12) Chambers, R. D. *Fluorine in Organic Chemistry*; Wiley: New York, 1973; Chapter 5, p 148.

(13) (a) Brown, S. H.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2935. (b) Cvetanovic, R. J. *Prog. React. Kinet.* **1963**, *2*, 39. (c) Calvert, J. G.; Pitts, J. N. *Photochemistry*; Wiley: New York, 1966, pp 60–166. (d) Gunning, H. E.; Strausz, O. P. *Adv. Photochem.* **1963**, *2*, 209.

(14) Callear, A. B.; Freeman, C. G. *Chem. Phys.* **1977**, *23*, 343.

(15) (a) Siegbahn, P., personal communication, 1995. (b) Winn, J. S. *Physical Chemistry*; Harper, Collins: New York, 1995; p 213.

(16) Costello, C. A.; McCarthy, T. J. *Macromolecules* **1984**, *17*, 2940; **1987**, *20*, 2819. Iqbal, Z.; Ivory, D. M.; Subota, J. S.; Elsenbaumer, R. L.; Bochman, R. H. *Macromolecules* **1986**, *19*, 2992.