J. Am. Chem. Soc. **1996,** *118,* 2525−2526 2525

Photoinduced Catalytic Defluorination of Perfluoroalkanes To Give Perfluoroalkenes

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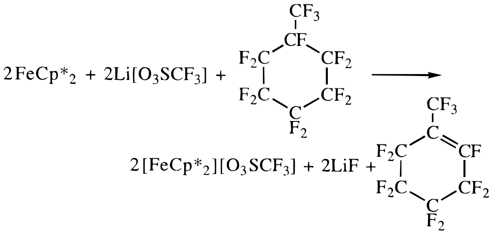
Received November 27, 1995

Fluoroorganic compounds are of current interest in connection with their important industrial applications[1] and the ozone depletion potential of CFCs.[2] Saturated perfluorocarbons are extremely inert,[3a] and few reactions are known.[3b−k] Reactions with strong reducing agents such as alkali or alkali earth metals are difficult to control and lead to complete mineralization.[3b,c] Controlled defluorinations have been observed with d-[3f,g] and f-block[3e] metal complexes, in one case[3g] giving a perfluoroarene. A radical anion has also been shown to aromatize cyclic perfluorocarbons.[3h] Very recently, we proposed[4] that Hg-photosensitized reduction of perfluoroalkanes by NH_3 gives the perfluoroalkene as an intermediate, which rapidly reacts with NH_3 to give perfluoroimines and perfluoronitriles. Perfluoroalkenes are also plausible intermediates in some prior reduction reactions,[3g,h] and are formed[3j,k] by photoinduced electron transfer from amines, but only where the substrate has two vicinal tertiary C−F bonds.

In many prior cases, complete reduction to the aromatic perfluorocarbon is observed. Stopping at the earlier perfluoroalkene stage is a serious challenge since the alkenes are known to be even more reactive toward electron transfer reactions than are their aromatic counterparts.[5] Perfluoroalkenes are valuable intermediates,[6] but there is still no general method to obtain them from the readily available saturated perfluoroalkanes. We now report such a reaction.

We have adopted decamethylferrocene ($FeCp^*_2$) as a photosensitizer, because it is nonnucleophilic and the oxidized form is easily reduced by Zn, making catalysis feasible. A Li salt, previously used by Richmond and co-workers,[3g] is required for reaction and acts as an F^- ion acceptor from the substrate. Finally, the polar solvent THF favors the photoinduced charge transfer chemistry.

In a stoichiometric version of the reaction, a solution of purified[7] perfluoromethylcyclohexane (C_7F_{14}, 4.00 g, 11.43 mmol), $FeCp^*_2$ (100 mg, 0.300 mmol), and $Li[O_3SCF_3]$ (1.30 g, 8.33 mmol) in dry THF (10 mL) was irradiated (17 h, medium pressure 200 W Hg lamp, Pyrex vessel) under N_2. After 30 min, the color changed from the yellow color of $FeCp^*_2$ to the green color of the ferricinium ion. After 17 h, the mixture contained unreacted $FeCp^*_2$ (40 mg, 0.120 mmol) and $[FeCp^*_2][O_3SCF_3]$ (90 mg, 0.180 mmol). The condensed volatiles consisted of a THF solution of the C_7F_{14} and 1-perfluoromethylcyclohexene, as shown by the appearance of a band at 262 nm ($\epsilon = 17\,000$) in the UV spectrum and of the characteristic[8] ^{19}F NMR resonances. Isolation of the alkene proved difficult because of the large excess of C_7F_{14}, but we were able to use the product mixture for the synthesis and isolation of perfluoroalkene derivatives. For example, reaction with NH_3 (1 atm, 60 min) gave **1** (26.0 mg, 90.0 μmol), previously synthesized[9a] from the alkene. Purification of the solids either by chromatography (TLC on alumina, CH_2Cl_2 eluent $R_f = 0.6$) or by recrystallization from CCl_4 yielded pure **1**. The physical data proved to be identical (MS, UV, IR, ^1H NMR, ^{19}F NMR, mp) with those previously reported for **1**.[9c] We find that 2 mol of ferricinium salt are formed per mole of perfluoroalkene, so the equation is



(1)

An excess of C_7F_{14} was necessary for the desired perfluoroalkene to be formed. Reduction to the perfluoroarene was not our goal since we recently reported[10] very efficient aromatization of saturated cyclic perfluorocarbons.

We verified that the ferricinium salt is readily and quantitatively reduced by granular Zn in THF. This allowed us to effect catalytic reduction of the perfluoroalkane, by irradiating a mixture of C_7F_{14} (6 g, 17.14 mmol), $FeCp^*_2$ (2.0 mg, 6.1 μmol), and $Li[O_3SCF_3]$ (1.30 g, 8.33 mmol) in 30 mL dry THF in the

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(1) (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 *Prepararion, 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. (d) Banks, R. E., Smart, B. E., Tatlow, J. C., Eds. *Organofluorine Chemistry. Principles and Commercial Applications*; Plenum Press: New York, 1994.

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(5) (a) Compare the electron affinities of hexafluorobenzene (0.51 eV) and perfluorocyclohexene (>1.4 eV). (b) Chowdhury, S.; Grimsrud, E. P.; Heinis, T.; Kebarle, P. *J. Am. Chem. Soc.* **1986**, *108*, 3630. (c) Drzaic, P. S.; Marks, J.; Brauman, J. I. In *Gas Phase ion Chemistry*; Bowers, M. T., Ed.; Academic Press: Orlando, FL, 1984; Vol. 3, p 167.

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(7) Traces of unsaturated perfluorocarbons in commercial C_7F_{14} (Aldrich) were eliminated by reaction with *n*-$BuNH_2$. After filtration of the fluoroimines and *n*-$BuNH_3F$, the material was washed with 1.0 M HCl and then with water. C_7F_{14} was then dried over $MgSO_4$ and distilled (59−61 °C). The UV spectra of all starting materials showed that unsaturation was completely absent.

(8) (a) Observed: −136.3 (CF_2, 2F), −136.2 (CF_2, 2F), −122.1 (CF_2, 2F), −112.3 (C-F, 1F), −112.0 (CF_2, 2F), −61.1 (CF_3, 3F). Literature: −136.4 (CF_2), −135.9 (CF_2), −121.3 (CF_2), −115.4 (C-F), −110.9 (CF_2), −61.3 (CF_3). (b) Dungan, C. H.; Van Wazer, J. R. *Compilation of Reported ^{19}F NMR Chemical Shifts*; Wiley-Interscience: New York, 1970. (c) Campbell, S. F.; Hudson, A. G.; Mooney, E. F.; Pedler, A. E.; Stevens, R.; Wood, K. N. *Spectrochim. Acta* **1967**, *23A*, 2119.

(9) (a) Derek, J.; Burdon, J.; Carter, P. A.; Patrick, C. R.; Tatlow, J. C. *J. Fluorine Chem.* **1982**, *21* (3), 305. (b) Doyle, A. M.; Pedler, A. E. *J. Chem. Soc. C* **1971**, 282. (c) MS (70 eV): 286 (M^+), 267 ($M^+ - F$), 186 ($M^+ - C_2F_4$). ^1H NMR (CD_2Cl_2): 5.75 (2H), 10.5 (1H). ^{19}F NMR (CD_2Cl_2): −57.8 (3F), −117.9 (2F), −123.0 (2F), −136.6 (2F). IR (NaCl film): 3505 (NH), 3345 (NH), 1676 (C=C), 1611 (NH), 1268 (CF), 1096 (CF). UV (EtOH): 274 (21800). Mp = 99−100 °C. Crystals of this compound can also be obtained by slow evaporation of a CH_2Cl_2 solution.

(10) Burdeniuc, J.; Crabtree, R. H. *Science* **1996**, *271*, 340.

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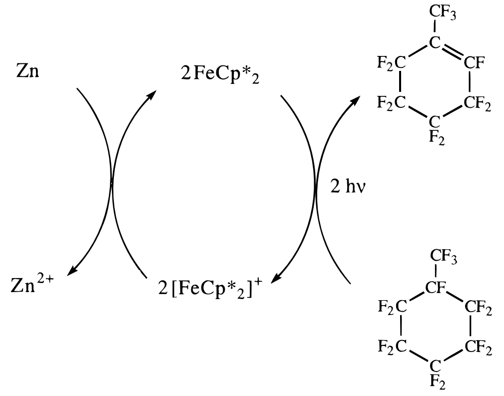
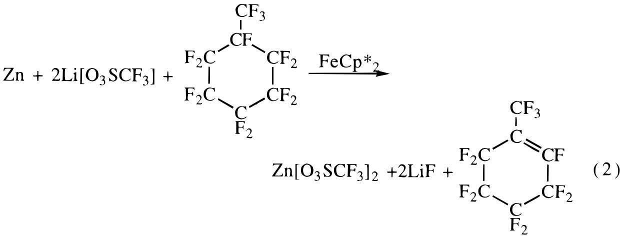
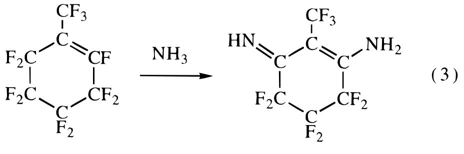


Figure 1.

presence of Zn (0.50 g, 7.6 mmol).[11] After 40 h, **1** was isolated (190 mg, 0.67 mmol) after treatment with NH_3 (110 turnovers (t.o.), 3.9% conversion, 96% yield). Figure 1 shows the catalytic cycle.



Conversion can be maximized (11.9%) by using C_7F_{14} (4.00 g, 11.43 mol), $FeCp*_2$ (100 mg, 0.30 mmol), and $Li[O_3SCF_3]$ (1.30 g, 8.33 mmol) in dry THF (10 mL) and irradiating for 19 h. As before, compound **1** (0.39 g, 1.36 mmol) was isolated after reaction with NH_3. The catalyst can be recovered in 90% yield. Attempts to increase the conversion gave byproducts that are still under study; no aromatics were found, however.



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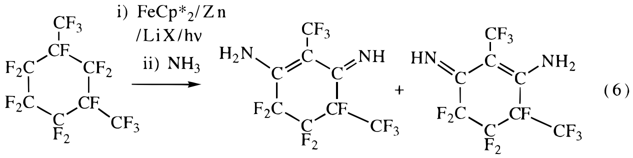
Perfluoro-2-methylpentane is also catalytically reduced (40 t.o.) to the corresponding trisubstituted perfluoroalkene,[14] (eq 4) suggesting initial attack at the tertiary CF bond.

$$(CF_3)_2CF-CF_2CF_2CF_3 + Zn + 2LiX \xrightarrow{FeCp*_2} (CF_3)_2C{=}CFCF_2CF_3 + ZnX_2 + 2LiF \quad (4)$$

Unlike in prior systems,[3k] there is no need that both CF bonds be tertiary. Perfluoro-2-methyl-2-pentene (**2**) was identified in the THF solution from the UV and ^{19}F NMR spectra,[12a] and the derivative **3** was isolated[13] after reaction with NH_3.

$$(CF_3)_2C{=}CFCF_2CF_3 + 10NH_3 \rightarrow (CN)_2C{=}C(NH_2)CF_2CF_3 + 7NH_4F \quad (5)$$

Perfluoro-1,3-dimethylcyclohexane was also catalytically reduced (60 t.o.),[15] and reaction with NH_3 gives a mixture of **4** and **4′**, identified from their physical data.[12b]



4 **4'**

We find that perfluoroalkenes are obtained from perfluoroalkanes by photoinduced electron transfer from $FeCp*_2$. In the presence of Zn, the reaction becomes catalytic because the ferricinium product of the photolysis is reduced to the starting $FeCp*_2$.

Acknowledgment. J.B. thanks 3M Corporation, and R.H.C. thanks the U.S. Department of Energy for funding. We also thank Kaprinidis and Turro for sending us a preprint of their article.

JA9539599

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[11] We avoided powdered Zn because it tends to absorb light.

[12] (a) ^{19}F NMR analysis of the THF/C_6H_6-d_6 solution showed new resonances at −59.41 (s, br, 3F), −61.9 (m, 3F), −85.1 (s, 3F), −118.5 (dd, J = 17.1, 1F), −98.8 (m, 2F) corresponding to perfluoro-2-methyl-2-pentene, as verified by comparison with a commercial sample (Aldrich). UV (THF) = 226 (110). (b) MS (70 eV): 336 (M^+), 317 ($M^+ - F$), 290 ($M^+ - F - CNH$), 186 ($M^+ - C_3F_6$), 166 ($M^+ - C_3F_6 - HF$). IR (NaCl film): 3570 (NH), 3448 (NH), 3350 (NH), 3180 (NH), 1652 (C=C), 1614 (NH), 1310 (CF), 1266 (CF), 1218 (CF), 1133 (CF). ^{19}F NMR (CCl_2D_2): −57.0 (CF_3, 3F), −57.5 (CF_3, 3F), −70.4 (CF_3, 3F), −74.2 (CF_3, 3F), −106.1 (d, $J_{FF}{}^{g}$ = 290 Hz, 1F, CF_2), −107.8 (d, $J_{FF}{}^{g}$ = 290 Hz, 1F, CF_2), −115.6 (d, $J_{FF}{}^{g}$ = 297 Hz, 1F, CF_2), −115.8 (d, $J_{FF}{}^{g}$ = 293 Hz, 1F, CF_2), −119.8 (d, $J_{FF}{}^{g}$ = 290 Hz, 1F, CF_2), −122.6 (d, $J_{FF}{}^{g}$ = 270 Hz, 1F, CF_2), −123.0 (d, $J_{FF}{}^{g}$ = 290 Hz, 1F, CF_2), −130.7 (d, $J_{FF}{}^{g}$ = 290 Hz, 1F, CF_2), −184.6 (m, br, CF, 1F), −184.9 (m, br, CF, 1F). 1H NMR (CCl_2D_2): 5.7 (br, 2H), 10.6 (br, 1H). UV (EtOH): 274 (16 400).

[13] Josey, A. D. *J. Org. Chem.* **1964**, *29*, 707.

[14] Experimental procedure: perfluoro-2-methylpentane (6.00 g, 17.7 mmol), $FeCp*_2$ (2.0 mg, 6.1 μmol), and $Li[O_3SCF_3]$ (1.30 g, 8.33 mmol) are dissolved in dry THF (30 mL) and irradiated for 40 h. Perfluoro-2-methyl-2-pentene (**2**, 72.0 mg, 0.240 mmol) was produced (75% yield, 1.36% conversion, 40 turnovers) which was converted into the isolable derivative $(CN)_2C{=}C(NH_2)CF_2CF_3$ (**3**, 50 mg, 0.24 mmol) by reaction with NH_3.

[15] Perfluoro-1,3-dimethylcyclohexane (6.00 g, 15.0 mmol), $FeCp*_2$ (2.0 mg, 6.1 μmol), and $Li[O_3SCF_3]$ (1.30 g, 8.33 mmol) are dissolved in dry THF (30 mL) and irradiated for 48 h. A mixture of isomers **4** and **4′** was obtained after reaction with NH_3 in a 60% yield (2.7% conversion from perfluoroalkane). Conversion was maximized (10%) by using $FeCp*_2$ (100 mg, 0.300 mmol) in 10 mL of dry THF together with $Li[O_3SCF_3]$ (1.30 g, 8.33 mmol) and perfluoro-1,3 dimethylcyclohexane (4.00 g, 10.0 mmol) and irradiating for 17 h. $FeCp*_2$ was recovered (95% yield), and reaction with NH_3 gave **4** and **4′** (310 mg, 0.93 mmol, 60%).