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PRELIMINARY NOTE

N-Halogeno-compounds. Part V [1]. Direct Conversion of Perfluoro-N-fluoro-piperidine and -morpholine into the Corresponding N-H Compounds [2]

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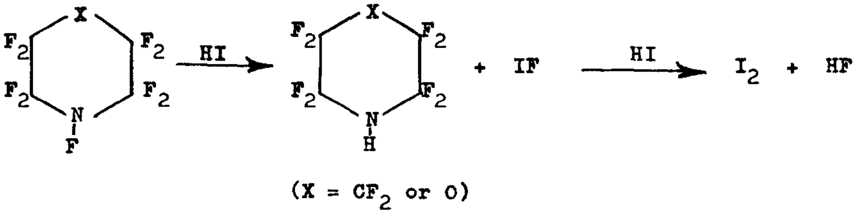
Anhydrous hydrogen iodide smoothly reduces perfluoro-N-fluoropiperidine to perfluoropiperidine (Scheme 1, X = CF_2), an amine obtained hitherto via treatment of its N-fluoro analogue with hydridopentacarbonylmanganese [3] or the two-stage procedure outlined in Scheme 2 (X = CF_2) [4]. This simple new method, which originates from the iodimetric determination of "positive" fluorine in N-fluoro-compounds of the fluorocarbon class [5], has also been employed to convert perfluoro-N-fluoromorpholine into the corresponding secondary amine (Scheme 1, X = O), a derivative first procured using hydridopentacarbonylmanganese (Scheme 2, X = O) [3].

Thus, distillation of the volatile product obtained by storing (24 h at 20 °C in the dark) a mixture of perfluoro-N-fluoropiperidine (5.8 g, 20.5 mmol) [6] and anhydrous hydrogen iodide (5.1 g, 40 mmol)



SCHEME 1

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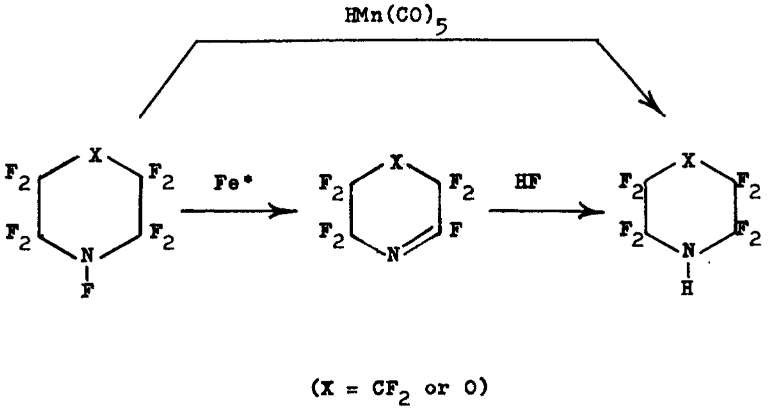
in a silica ampoule (300 cm^3, "flamed out" in vacuo prior to use) under anaerobic conditions gave perfluoropiperidine (4.35 g, 16.4 mmol) in 80% yield; the solid product contained iodine (14.9 mmol, 74%; estimated using $Na_2S_2O_3$). The yield of perfluoropiperidine rose to 99% and that of iodine to 95% when the reaction was repeated ($C_5F_{10}NF$ 12.9 mmol, HI 25.0 mmol) in the presence of a molecular sieve (3 g ; Type 4A, Linde Air Products, dried in vacuo before use) to absorb hydrogen fluoride and any water produced through attack of the former on the reaction vessel. When a mixture of perfluoro-N-fluoromorpholine (3.3 g, 13.2 mmol), anhydrous hydrogen iodide (3.4 g, 26.4 mmol), and Type 4A molecular sieve (3 g) was stored, as above, for 7 days, the product contained perfluoromorpholine (1.3 g, 5.6 mmol, 43%), perfluoro-5,6-dihydro-2H-1,4-oxazine (0.75 g, 3.6 mmol, 27% ; i.e., dehydrofluorination of the amine occurred), perfluoro-N-fluoromorpholine (0.2 g, 0.8 mmol, 6% recovery), silicon tetrafluoride, iodine, and perfluoro-oxydiacetic acid (a product known to be formed by hydrolysis of the oxazine [9]).



SCHEME 2

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* Mercury [7] or triphenylphosphine [8] is a better reagent.

1 Part IV, R. E. Banks, M. G. Barlow, and M. M. Saleh, J. Fluorine Chem., 10 (1977), 81.

2 See R. E. Banks, 'Fluorocarbons and their Derivatives', Macdonald, London, 1970 (2nd. edn.), p. 125, for the initial disclosure.

3 R. E. Banks, R. N. Haszeldine, and R. Hatton, J. Chem. Soc. (C), (1967) 427.

4 R. E. Banks, W. M. Cheng, and R. N. Haszeldine, J. Chem. Soc., (1964) 2485.

5 R. E. Banks and E. D. Burling, J. Chem. Soc., (1965) 6077.

6 Prepared by Simons' electrochemical fluorination of pyridine [R. E. Banks, A. E. Ginsberg, and R. N. Haszeldine, J. Chem. Soc., (1961) 1740].

7 R. E. Banks and G. E. Williamson, J. Chem. Soc., (1965) 815.

8 R. E. Banks, K. Mullen, W. J. Nicholson, C. Oppenheim, and A. Prakash, J. Chem. Soc. Perkin Trans. I, (1972) 1098. Note that toluene may be used as solvent instead of benzene.

9 See ref. 5, which also gives details of the method used to prepare the perfluoro-*N*-fluoromorpholine used in this work, *viz.* Simons' electrochemical fluorination of morpholine.