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SYNTHESIS OF GROUP Vb FLUORIDES FROM N-FLUORO-COMPOUNDS

R.E. Banks, R.N. Haszeldine, and R. Hatton

Department of Chemistry, University of Manchester Institute
of Science and Technology, Manchester, 1.

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Although 2,6-dimethylpiperidine, 2,2,6,6-tetramethylpiperidine, and 2,2,6,6-tetramethylpiperid-4-one react with perchloryl fluoride to give the corresponding N-fluoro-compounds, piperidine yields N-perchlorylpiperidine rather than N-fluoropiperidine.(1,2) The last compound has now been obtained in 9% yield by the slow addition of piperidine to an equimolar amount of perfluoro-N-fluoropiperidine in light petroleum† at room temperature; piperidine hydrofluoride, unchanged perfluoro-N-fluoropiperidine (not estimated), and 3,3,4,4,5,5,6,6-octafluoro-2-(N-piperidyl)-3,4,5,6-tetrahydropyridine (I) (25%) are also isolated. Analytically-pure N-fluoropiperidine, b.p. 40-44°/70 mm., liberates iodine readily from acidified potassium iodide solution. Its ^{19}F n.m.r. spectrum consists of a broad singlet at $-55{\cdot}8$ p.p.m. downfield from external trifluoroacetic acid, while its ^{1}H spectrum shows three absorption systems of relative intensities 1:1:3 at 3·2, 4·0, and 5·2 p.p.m. to high field of benzene (interchange reference), the first two of which are assigned to axial and equatorial α-protons rendered non-equivalent by slow inversion at the nitrogen and/or slow ring-inversion. As expected, the i.r. spectrum of N-fluoropiperidine shows no N-H absorption at ca. 3·0μ, but a strong band assigned to the >NF group appears at 11·2μ. Compound (I) can be obtained in 85% yield by treatment of perfluoro-3,4,5,6-tetrahydropyridine (II) (3,4) with piperidine at -20 to 23° (Scheme 1).

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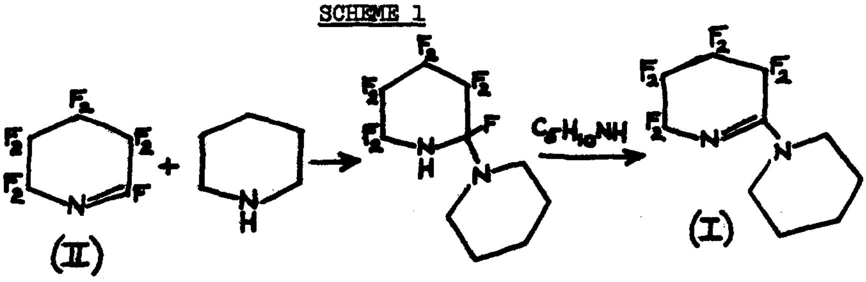
† CAUTION! Piperidine reacts violently with undiluted perfluoro-N-fluoropiperidine at room temperature.

SCHEME 1

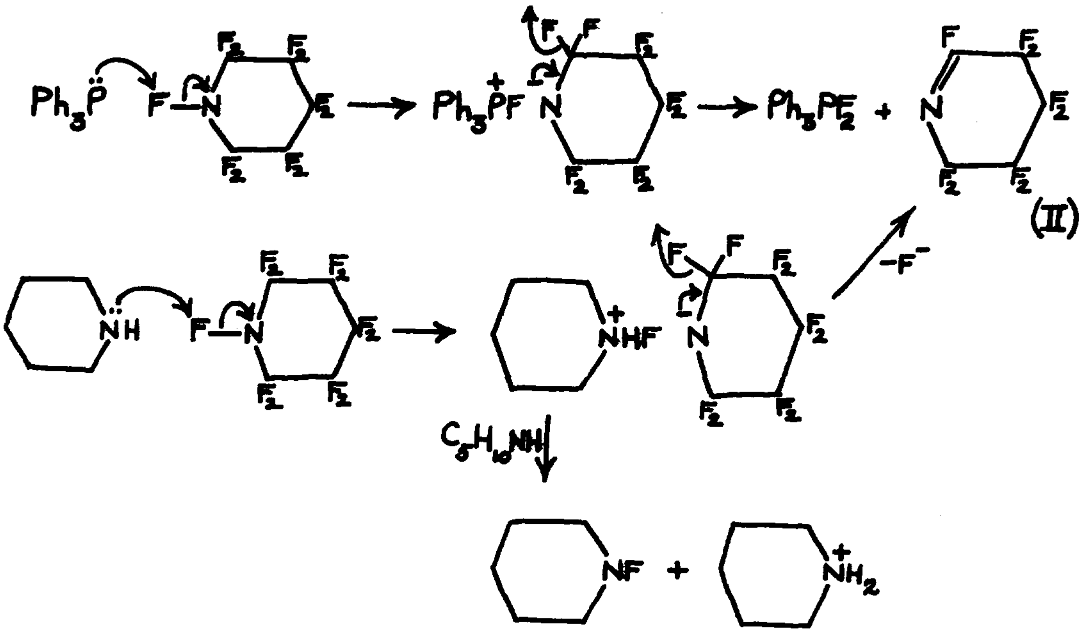


Similarly, reaction of perfluoro-*N*-fluoropiperidine with triphenylphosphine, -arsine, or -stibine in benzene solution at room temperature provides the known difluorides Ph_3PF_2, Ph_3AsF_2, Ph_3SbF_2 in good yields (84, 81, and 69% respectively), and the *N*-fluoro-compound is defluorinated to perfluoro-3,4,5,6-tetrahydropyridine in 91, 98, and 72% yield, respectively.

Difluorotriphenylphosphorane (56%) is also formed, together with nitrogen (64%) and unidentified material, when a solution of triphenylphosphine in benzene is shaken with nitrogen trifluoride, which, unlike perfluoro-*N*-fluoropiperidine, is available commercially. Fluorination of tris(dimethylamino)phosphine with nitrogen trifluoride at 20–45° in the absence of solvent gives the phosphorane $(Me_2N)_3PF_2$ in 80% yield,(5) and there seems no reason why similar derivatives of arsenic and antimony should not be prepared by this method.

Since perfluoro-(*N*-cyclobutylpiperidine), obtained by photolysis of perfluoro-*N*-fluoropiperidine with perfluorocyclobutene,(6) reacts with neither piperidine nor triphenylphosphine under conditions where perfluoro-*N*-fluoropiperidine does quite readily, and since good evidence has been obtained(7) for attack by iodide ion(3) or propane-2-nitronate ion(8) on the fluorine of the >NF group in perfluoro-*N*-fluoropiperidine, mechanisms of the type shown in Scheme 2 are suggested for the above fluorinations effected with perfluoro-*N*-fluoropiperidine. It is possible that an analogous mechanism (Scheme 3) is operative for the reactions involving nitrogen trifluoride, which was shown long ago(9) to react with hydriodic acid according to the equation $NF_3 + 6HI \longrightarrow NH_3 + 3I_2 + 3HF$. Evidence for the formation of fluoronitrene in the reaction between nitrogen trifluoride and triphenylphosphine is being sought.

SCHEME 2



SCHEME 3

$$Ph_3\ddot{P}\ F{-}NF_2 \longrightarrow [Ph_3\overset{+}{P}F\ \overset{-}{N}F_2] \longrightarrow Ph_3PF_2 + :NF \longrightarrow FN{:}NF$$

$$Ph_3\ddot{P}\ F{-}N{:}NF \longrightarrow [Ph_3\overset{+}{P}F\ \overset{-}{N}{:}NF] \longrightarrow Ph_3PF_2 + N_2$$

The identities of the known difluorides R_3MF_2 (R = Ph, M = P, As, or Sb; R = Me_2N, M = P) were confirmed by elemental analysis and measurement of their physical and spectroscopic properties.

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