

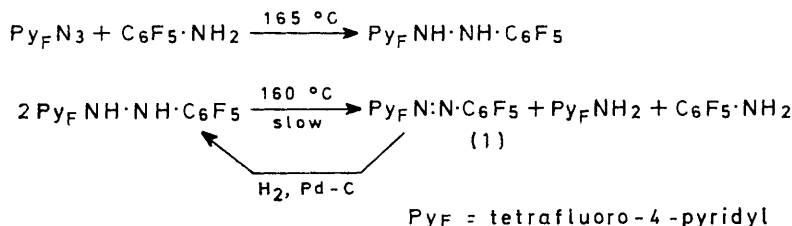
Heterocyclic Polyfluoro-compounds. Part XXII.¹ Synthesis of Octafluoro-4,4'-azopyridine and Tetrafluoro-4-(pentafluorophenylazo)pyridine

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Thermolysis of 4-azidotetrafluoropyridine in the presence of pentafluoroaniline yields tetrafluoro-4-(pentafluorophenylazo)pyridine and *N*-(pentafluorophenyl)-*N'*-(tetrafluoro-4-pyridyl)hydrazine; catalytic hydrogenation of the former product yields the latter, which decomposes into 4-aminotetrafluoropyridine, pentafluoroaniline, and the azo-compound at 160 °C *in vacuo*. Octafluoro-4,4'-azopyridine can be obtained by pyrolysis of 4-(dichloroamino)tetrafluoropyridine, prepared by treatment of 4-aminotetrafluoropyridine with *t*-butyl hypochlorite.

HITHERTO no polyfluorinated azopyridines have been described,[†] despite the considerable effort spent on the study of polyfluoropyridine chemistry during the past sixteen years.⁴ The first compound of this class, the unsymmetrical tetrafluoro-4-(pentafluorophenylazo)pyridine (1), was obtained from an experiment designed to throw light on the mechanism of formation of decafluoroazobenzene during thermolysis of azidopentafluorobenzene in the presence of an excess of pentafluoroaniline:³ decomposition of 4-azidotetrafluoropyridine at

with bleaching powder in boiling carbon tetrachloride (*i.e.* by methods used to convert pentafluoroaniline into decafluoroazobenzene⁹) proved abortive.¹⁰ However, the required conversion was easily effected by a stepwise procedure (Scheme 2) which provided octafluoro-4,4'-azopyridine in >40% yield. 4-(Dichloroamino)tetrafluoropyridine, the intermediate in this route, is an easily isolable, high boiling, pale yellow liquid; it rapidly oxidises iodide ion (sodium iodide in wet acetone) to iodine at room temperature and decomposes into the

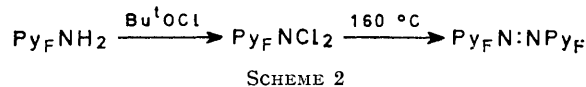


SCHEME 1

165 °C in the presence of a *ca.* ten-molar excess of pentafluoroaniline gave tetrafluoro-4-(pentafluorophenylazo)pyridine in 24% yield but no octafluoro-4,4'-azopyridine, providing evidence for the unimportance of nitrene dimerization or nitrene-azide interaction (*cf.* ref. 5) in such systems. Additionally, it proved possible in the azidopyridine case to isolate a small amount (4.5% yield) of the proposed,³ hydrazo-precursor of azo material; as expected,^{6,7} it disproportionated when heated *in vacuo*, giving the azo-compound (1), pentafluoroaniline, and 4-aminotetrafluoropyridine in approximately theoretical amounts (see Scheme 1).

Attempts to prepare octafluoro-4,4'-azopyridine by oxidation of the easily procured⁸ 4-aminotetrafluoropyridine with lead tetra-acetate in boiling benzene or

corresponding azo-compound and chlorine only slowly at 100 °C, thus resembling *NN*-dichloropentachloroaniline.¹¹ 4-(Dichloroamino)tetrafluoropyridine is the



first polyfluorinated *N*-chloroarylamine to be reported, and we have adapted its mode of preparation to obtain a range of carbocyclic analogues of type 4-XC₆F₄NCl₂, the detailed chemistry of which is receiving attention.

EXPERIMENTAL

I.r., ¹⁹F n.m.r. (trifluoroacetic acid as external reference, shifts to high field designated positive), and mass spectra

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⁷ E. T. McBee, G. W. Calundann, C. J. Morton, T. Hodgins, and E. P. Wesseler, *J. Org. Chem.*, 1972, **37**, 3140.

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[†] The formation of tetrafluoro-4-(pentafluorophenylazo)pyridine from 4-azidotetrafluoropyridine and pentafluoroaniline was disclosed earlier, but no details were given.^{2,3}

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³ R. E. Banks, 'Fluorocarbons and their Derivatives,' 2nd edn., Macdonald, London, 1970, p. 222; R. E. Banks and M. G. Barlow, 'Fluorocarbon and Related Chemistry,' Chemical Society Specialist Periodical Report, 1971, vol. 1, p. 248; W. T. Flowers, *ibid.*, 1974, vol. 2, p. 439; G. G. Yakobson, T. D. Petrova, and L. S. Kobrina, *Fluorine Chem. Rev.*, 1974, **7**, 115.

⁴ R. E. Banks and A. Prakash, *Tetrahedron Letters*, 1973, 99.

were obtained with a Perkin-Elmer spectrophotometer model 257, a Perkin-Elmer R10 (56.46 MHz) or Varian HA-100 (94.10 MHz) instrument, and a G.E.C.-A.E.I. MS902 spectrometer (electron beam energy 70 eV), respectively.

Pentafluoroaniline was used as received from Fluorochem Ltd. (Glossop, Derbyshire), 4-amino-⁸ and 4-azido-tetrafluoropyridine¹² were synthesised *via* pentafluoropyridine, and *t*-butyl hypochlorite was prepared by treating *t*-butyl alcohol with commercial bleach solution.¹³

Tetrafluoro-4-(pentafluorophenylazo)pyridine.—A flask (250 cm³) containing a solution of 4-azidotetrafluoropyridine (1.5 g, 7.8 mmol) in pentafluoroaniline (15 g, 82 mmol) and a PTFE-encapsulated magnet, and connected to a nitrometer *via* a water-cooled reflux condenser, was flushed with nitrogen to remove air then lowered (behind a blast screen) into an oil-bath kept at 165 °C by a combined hot-plate-magnetic stirrer. Evolution of nitrogen appeared to cease after 4.5 h. The black tarry product was fractionally sublimed *in vacuo* (−78 °C condenser) to give pentafluoroaniline (bath temp. 20–40 °C; 7.1 g, 47% recovery), a bright orange solid (60–70 °C; 1.35 g), and a pale orange solid (80–100 °C; 0.94 g); the black residue (Found: C, 41.3; H, 0.9; F, 42.9; N, 12.1%) did not melt when heated to 350 °C. Subjection of the orange fractions to adsorption column chromatography (silica, 1 m × 11 mm, eluted with carbon tetrachloride–chloroform mixtures) provided *tetrafluoro-4-(pentafluorophenylazo)pyridine* (0.65 g, 1.9 mmol, 24%) (Found: C, 38.1; F, 48.5; N, 12.0%; *M*⁺, 345. C₁₁F₉N₃ requires C, 38.3; F, 49.5; N, 12.2%; *M*, 345) as bright orange crystals, m.p. 122 ± 0.5 °C, δ_F (ca. 20% w/v soln. in Me₂CO) +14.4 (2-, 6-F), +73.4 (2', 4', 6'-F), +78.6 (3-, 5-F), and +88.4 p.p.m. (3', 5'-F) (rel. int. 2 : 3 : 2 : 2), and *N-(pentafluorophenyl)-N'-(tetrafluoro-4-pyridyl)hydrazine* (0.12 g, 0.35 mmol; 4.5%) (Found: C, 38.5; H, 0.8; F, 50.0; N, 11.9%; *M*⁺, 347. C₁₁H₂F₉N₃ requires C, 38.1; H, 0.6; F, 49.3; N, 12.1%; *M*, 347) as fine needles, m.p. 106–107 °C, λ_{max} (mull) 2.99 and 3.04 μm (N–H str.), δ_F (Me₂CO soln.; 94.1 MHz spectrum, *p*-CF₃·S·C₆H₄Cl lock signal, observed shifts converted to ext. CF₃·CO₂H scale by subtracting 35.5 p.p.m.) +17.6, +84.5 (2-, 6-F and 3-, 5-F, respectively, of the tetrafluoropyridyl group), +81.0, +87.5, and +91.5 p.p.m. (2-, 6-F, 3-, 5-F, and 4-F, respectively, of the pentafluorophenyl group) (rel. int. 2 : 2 : 2 : 2 : 1).

Hydrogenation of Tetrafluoro-4-(pentafluorophenylazo)pyridine.—The azo-compound (0.50 g, 1.45 mmol) in light petroleum (b.p. 60–80 °C)–diethyl ether (1 : 1 v/v; 30 cm³) was hydrogenated over 10% palladium-charcoal at 21 °C and atmospheric pressure. Work-up by standard techniques gave the hydrazo-compound (0.32 g, 0.92 mmol; 63%) (after recrystallisation from light petroleum), m.p. and

mixed m.p. 106.5–107.5 °C, identical (i.r. spectrum) with the material described above.

Thermolysis of *N-(Pentafluorophenyl)-N'-(tetrafluoro-4-pyridyl)hydrazine.*—The hydrazo-compound (0.047 g, 0.136 mmol) was heated in the absence of air at 160 °C for 24 h in a Pyrex ampoule (300 cm³). The product was dissolved in methanol (10.00 cm³) and the solution was shown by analytical high pressure liquid chromatography (Du Pont liquid chromatograph model 830 fitted with 0.5 m ETH and ODS Permaphase columns) to contain pentafluoroaniline (0.035 mmol, 25%), 4-aminotetrafluoropyridine (0.030 mmol, 21%), tetrafluoro-4-(pentafluorophenylazo)pyridine (0.074 mmol, 53%), and traces of several unknown compounds.

4-(Dichloroamino)tetrafluoropyridine.—A solution of 4-aminotetrafluoropyridine (6.0 g, 36.1 mmol) in chloroform (50 cm³) was added slowly to a cold (−15 °C) solution of *t*-butyl hypochlorite (8.6 g, 86.6 mmol) in carbon tetrachloride (250 cm³). The mixture was stirred at −15 °C for 6 h, during which time samples were analysed by i.r. spectroscopy at hourly intervals; no change occurred, so the temperature was raised in 20 °C stages (sampling was continued) until the solvent mixture boiled. After 4 h under reflux, no free amine could be detected by i.r. spectroscopy; the product was evaporated at 40 °C under reduced pressure, and the involatile residue was fractionated in a semi-micro Vigreux still to provide *4-(dichloroamino)tetrafluoropyridine* (5.0 g, 21.3 mmol, 59%) (Found: C, 26.0; Cl, 29.8; F, 33.3; N, 11.2. C₅Cl₂F₄N₂ requires C, 25.5; Cl, 30.2; F, 32.3; N, 11.9%), a pale yellow oil, b.p. 44–45 °C at 3–4 mmHg, δ_F (neat liq.) +9.8 (2-, 6-F), and +65.4 p.p.m. (3-, 5-F) (rel. int. 1 : 1). A purer sample [judged by the analytical data (Found: C, 25.9; Cl, 30.2; F, 31.9; N, 11.6%)] of the dichloroamino-compound was obtained by treating the distilled material as follows: a sample (3.0 g) was added to an equimolar proportion of toluene (1.17 g) in light petroleum (b.p. 30–40 °C; 25 cm³) and the mixture was cooled to −78 °C; the solid complex which precipitated was isolated by filtration at −78 °C then warmed to room temperature, and the toluene released was pumped away.

Octafluoro-4,4'-azopyridine.—A sample (1.0 g, 4.3 mmol) of 4-(dichloroamino)tetrafluoropyridine purified by distillation was heated at 160 °C for 4 h. The deep red product solidified when cooled, and was recrystallised from light petroleum (b.p. 60–80 °C) to give bright orange *octafluoro-4,4'-azopyridine* (0.5 g, 1.5 mmol, 70%) (Found: C, 36.4; F, 46.2; N, 17.0%; *M*⁺, 328. C₁₀F₈N₄ requires C, 36.6; F, 46.3; N, 17.1%; *M*, 328), m.p. 147–148 °C, δ_F (ca. 15% w/v soln. in Me₂CO) +13.0 (2-, 2', 6-, 6'-F) and +75.0 p.p.m. (3-, 3', 5-, 5'-F) (rel. int. 1 : 1).

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