338. *Heterocyclic Polyfluoro-compounds. Part I. Pentafluoropyridine.**

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Pentafluoropyridine has been prepared by defluorination of undecafluoropiperidine. Infrared spectroscopy reveals a characteristic ring vibration near 1497 cm.$^{-1}$ for pentafluoropyridine and suggests that appreciable aromatic character is associated with the ring.

THE literature contains reference to the preparation of only monofluoropyridines,[1,2] except for a claim concerning an unidentified difluoropyridine.[2] Pentafluoropyridine has now

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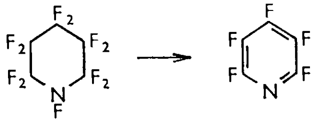
* Preliminary communication, *Proc. Chem. Soc.*, 1960, 211.

[1] Roe and Hawkins, *J. Amer. Chem. Soc.*, 1947, **69**, 2443; Simons, U.S.P. 2,447,717/1948; *J. Electrochem. Soc.*, 1949, **95**, 47; Hawkins and Roe, *J. Org. Chem.*, 1949, **14**, 328; Bradlow and Vanderwerf, *ibid.*, p. 509; Roe, Cheek, and Hawkins, *J. Amer. Chem. Soc.*, 1949, **71**, 4152; Minor, Hawkins, Vanderwerf, and Roe, *ibid.*, p. 1125; Beaty and Musgrave, *J.*, 1952, 875; Cava and Weinstein, *J. Org. Chem.*, 1958, **23**, 1616; Finger and Starr, *J. Amer. Chem. Soc.*, 1959, **81**, 2674.

[2] Simons and Herman, Abs. Amer. Chem. Soc. Meeting, Sept. 1947, p. 13J.

been prepared by defluorination of undecafluoropiperidine on a clean iron surface at 580—610°/<1 mm., with a particularly short contact time of ~1 sec.:



Undecafluoropiperidine is readily prepared, albeit in low yield, by the electrochemical fluorination of pyridine,[3] and hence a convenient two-stage conversion of pyridine into pentafluoropyridine can be effected.

The aromatisation of cyclic fluorocarbons by defluorination with hot nickel or, preferably, iron was first applied to the preparation of hexa- and penta-fluorobenzene from highly fluorinated cyclohexadienes.[4] The reaction was then extended to a range of alicyclic fluorocarbons and shown to provide a useful general route to aromatic fluorocarbons.[5] The defluorination of alicyclic fluorocarbons, however, requires the use of long contact times (10—30 min.) at atmospheric pressure. Thus, while octafluorotoluene is formed in 25% yield by defluorination of perfluoro(methylcyclohexane) at 500° at atmospheric pressure with a long contact time, we find that perfluoro(methylcyclohexane) is recovered unchanged after contact with iron at 700° for 1 sec. at 1 mm. pressure. Clearly, in the aromatisation of undecafluoropiperidine to pentafluoropyridine the N–F bond appreciably facilitates defluorination.

Pentafluoropyridine is a colourless, almost odourless, mobile liquid, b. p. 83·3°; as noted earlier,[6] replacement of a =CF– group by =N– in fluorocarbons has little effect on the boiling point (C_6F_6 has b. p. 81°). The aromatic character of pentafluoropyridine is revealed by the characteristic ring vibration at 1497 cm.$^{-1}$ in the infrared spectrum of its vapour, close to that (1536 cm.$^{-1}$) in hexafluorobenzene.[7]

Since the preliminary communication regarding this work, other workers [8] have reported the preparation of pentafluoropyridine in *ca.* 12% yield by defluorination of undecafluoropiperidine with nickel at 560° at atmospheric pressure.

EXPERIMENTAL

Preparation of Undecafluoropiperidine.—A 3·35 mole % solution of pyridine in anhydrous hydrogen fluoride was electrolysed at 25 amp. and 5·5 v (current density 0·0044 amp./cm.^{2}) in the electrochemical fluorination apparatus described previously.[9] After an induction period of *ca.* 400 amp. hr., during which free fluorine and/or oxygen difluoride was evolved from the cell, product began to collect at the rate of 8·96 g./Faraday in the trap cooled to −78°. Crude undecafluoropiperidine (yield, 8%), b. p. 46—55°, was separated from this product, which consisted mainly of perfluoropentane, by distillation through a 45 cm. × 1·2 cm. column packed with 2 mm. Fenske glass helices. Pure undecafluoropiperidine (Found: C, 21·1; N, 4·9%; *M*, 285. Calc. for $C_5F_{11}N$: C, 21·2; N, 4·95%; *M*, 283), b. p. 49°, was obtained from the crude material by means of large-scale gas chromatography (column, dinonyl phthalate–Celite; 75°; N_2 flow-rate, 10 l./hr.).

Preparation of Pentafluoropyridine.—The low-pressure defluorination apparatus is shown in Fig. 1. The pyrolysis section consisted of a nickel tube A (25″ long × 0·75″ i.d.) packed tightly with fine iron wire (100 g.) and heated electrically over 16″ of its length. The tube was connected to the " Pyrex " glass vacuum-system by means of adaptors (B) made from ⅞″ o.d. mild-steel " Ermeto " couplings (Fig. 2). The seals made by these couplings remained leak-free

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[3] Simons, U.S.P. 2,519,983/1950; Simmons *et al.*, *J. Amer. Chem. Soc.*, 1957, **79**, 3429.

[4] Banks, Barbour, Tipping, Gething, Patrick, and Tatlow, *Nature*, 1959, **183**, 586.

[5] Gething, Patrick, Stacey, and Tatlow, *Nature*, 1959, **183**, 588; Coe, Patrick, and Tatlow, *Tetrahedron*, 1960, **9**, 240.

[6] Haszeldine, *J.*, 1951, 102.

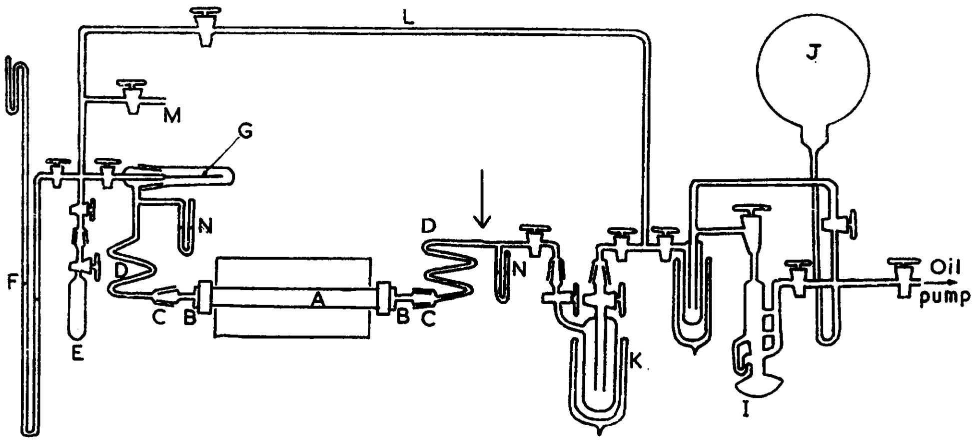
[7] Birchall and Haszeldine, *J.*, 1959, 13.

[8] Burdon, Gilman, Patrick, Stacey, and Tatlow, *Nature*, 1960, **186**, 231.

[9] Haszeldine and Nyman, *J.*, 1956, 2684.

even under a vacuum of 10^{-6} cm. Hg with the centre portion of the nickel tube at 800°. Heat conduction along the adaptors was almost eliminated by reducing the wall thickness of the stainless-steel tubing from $\frac{1}{8}''$ to $\frac{1}{50}''$ over a length of 1·5″. This enabled the final glass-to-metal joints (C) to be secured with picein. The flexible glass spirals (D) were necessary for the removal of the pyrolysis section from the vacuum line.

FIG. 1.



During a defluorination experiment, fluorocarbon contained in trap E under its own vapour pressure (measured by the manometer F) passed through the capillary G into the pyrolysis section, which was evacuated continuously by a mercury diffusion pump I backed by a 10 l. storage bulb J initially evacuated to 10^{-4} cm. Hg. E was immersed in a water-bath held at 25° to enable the perfluoropiperidine to evaporate at an approximately constant rate. The pressure in the pyrolysis tube was measured by the manometers N. The defluorination product was condensed in trap K which was cooled to −196°; uncondensed gases collected in bulb J. The line L enabled the product in trap K to be returned, if necessary, to trap E for re-cycling. Before each defluorination experiment, the iron wire was activated at 650°/10 mm. Hg by dry hydrogen which was metered slowly into the apparatus at M.

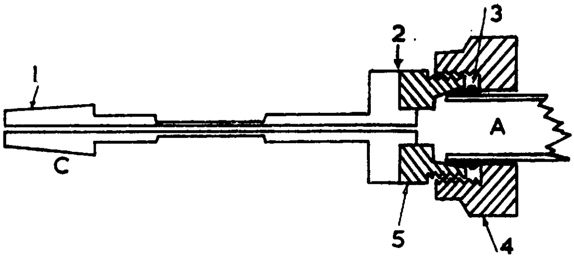


FIG. 2. 1, *Stainless steel,* B.14 *cone*; 2, *silver solder*; 3, "*Ermeto*" *ring*; 4, "*Ermeto*" *nut*; 5, *one half of an* "*Ermeto*" *coupling body.*

In a typical preparation of pentafluoropyridine, undecafluoropiperidine (6·2 g.) was defluorinated at 600°/<1 mm. Hg (contact time <1·7 sec.) to give an almost colourless liquid product (2·3 g.) shown by analytical gas chromatography (column, dinonyl phthalate–Celite) to consist mainly of three components, none of which was undecafluoropiperidine. The component with the longest retention time (35 min., compared with 2 min. 9 sec. and 2 min. 52 sec.) was *pentafluoropyridine* (Found: C, 35·6; N, 8·3%; *M*, 165. C_5F_5N requires C, 35·5; N, 8·3%; *M*, 169), m. p. −41·5°, n_D^{20} 1·3856, separated in 26% yield from the defluorination product by large-scale gas–liquid chromatography. The other 74% of the defluorination product contained unsaturated heterocyclic fluorocarbons.

The vapour pressure of pentafluoropyridine, measured over the temperature range 0—90°, is given by the equation $\log_{10} p = 8{\cdot}20 - 1898/T$, where p is in mm. The calculated b. p. is 83·3°, Trouton's constant is 24·4, and the latent heat of vaporisation is 8685 cal. mole.$^{-1}$.

Pentafluoropyridine was not formed when undecafluoropiperidine was defluorinated at 500°/221 mm. (contact time 4 min.), although the piperidine was completely converted into unsaturated heterocyclic fluorocarbons. For this experiment the capillary G was placed after the pyrolysis section at the position arrowed in Fig. 1, and the pressure in the pyrolysis tube was measured by manometer F. Defluorination of undecafluoropiperidine at $620°/<1$ mm. gave pentafluoropyridine in *ca.* 20% yield, but at $700°/<1$ mm. the organic material was almost completely destroyed and the iron became coated with a carbonaceous film.

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