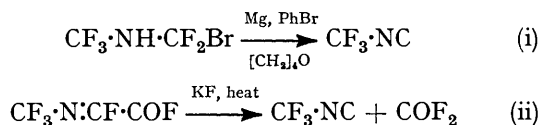


Polyfluoroarenes. Part XXI.¹ Synthesis, Decarbonylation, and Dehydration of 2',3',4',5',6'-Pentafluoroformanilide: Formation of Pentafluorophenyl Isocyanide

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Pentafluoroformanilide has been synthesised from ethyl formate and the monosodium salt of pentafluoroaniline; its spectroscopic properties are discussed, and its decarbonylation to pentafluoroaniline with hot calcium oxide and dehydration to pentafluorophenyl isocyanide with phosphorus pentoxide at 250 °C are described.

TRIFLUOROMETHYL ISOCYANIDE is the sole fluorocarbon isocyanide reported to date,† its synthesis having been achieved *via* two routes terminating, respectively, in the unusual elimination reactions (i)^{3a} and (ii).^{3b} The



possibility of converting pentafluoroaniline into pentafluorophenyl isocyanide *via* Hofmann's carbylamine reaction⁴ and α -elimination of water from *N*-substituted formamides⁵ has now been examined.^{6,7}

A carbylamine test⁸ with pentafluoroaniline rapidly created a nauseous smell and the i.r. spectrum of the complex liquid product contained a sharp absorption at 4.70 μm ; attempts to isolate pentafluorophenyl isocyanide (or a related isocyanide produced *via* displacement of nuclear fluorine by the basic reagents employed) from the products of preparative⁹ carbylamine reactions failed.⁷ ‡ Attention was therefore turned to the synthesis and dehydration of 2',3',4',5',6'-pentafluoroformanilide.

Pentafluoroformanilide was isolated in 55% yield following treatment of ethyl formate with the sodium salt of pentafluoroaniline¹¹ in tetrahydrofuran at -20 to 20 °C; pentafluoroaniline itself, being a poor nucleophile, reacted only sluggishly with ethyl formate even at 150 °C, giving the anilide in 30% yield (based on 33% conversion of the amine) after 24 h. Like formanilide, it is readily soluble in ethanol, acetone, diethyl ether, and chloroform but dissolves in water only on heating. Unlike formanilide, it is readily soluble in dilute aqueous alkali, presumably owing to the greater acidity of the hydrogen attached to nitrogen, and undergoes hydrolysis

† The only polyfluorinated alkyl isocyanide known, 2,2,2-trifluoroethyl isocyanide, can be obtained by dehydration of the appropriate formamide ($\text{CF}_3\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CHO}$) with the Ugi reagent $\text{COCl}_2\text{-Bu}_3\text{N}$.²

‡ This work was completed before the disclosure¹⁰ that the Hofmann carbylamine reaction is significantly improved by the use of phase-transfer catalysis.

¹ Part XX, J. M. Birchall, R. N. Haszeldine, and M. Wilkinson, *J.C.S. Perkin I*, 1974, 1740.

² A. P. Sergeev and M. A. Énglin, *Zhur. org. Khim.*, 1971, 7, 1078.

³ (a) S. P. Makarov, M. A. Énglin, A. F. Videiko, and T. V. Nikolaeva, *Zhur. obshchei Khim.*, 1967, 37, 2781; (b) R. E. Banks, R. N. Haszeldine, M. J. Stevenson, and B. G. Willoughby, *J. Chem. Soc. (C)*, 1969, 2119. For further information on $\text{CF}_3\cdot\text{NC}$ see refs. 4 and 5.

to pentafluoroaniline at elevated temperatures (hot dilute sulphuric acid effects the same change). Pentafluoroformanilide can be recovered quantitatively after slow passage through an evacuated silica tube at 500 °C; this, and the failure to obtain any pentafluorophenyl isocyanide by use of the dehydrating agents⁵ $\text{POCl}_3\text{-Bu}^t\text{OK}$ at 50 °C and $\text{COCl}_2\text{-Et}_3\text{N}$ at 0 °C, led to attempts to dehydrate pentafluoroformanilide with hot phosphorus pentoxide in a vacuum flow system so that the volatile products could be removed quickly from the reaction zone and shock cooled. Dehydration of *N*-mono-substituted formamides to isocyanides with phosphorus pentoxide in the presence of a base is known,⁵ but flow techniques do not appear to have been used previously.

Sublimation of pentafluoroformanilide into the mouth of a continuously evacuated Pyrex tube heated to 150 °C and containing a layer of phosphorus pentoxide taken straight from a fresh bottle without attempting to exclude atmospheric moisture gave only starting material contaminated with pentafluoroaniline, the expected product of acidic hydrolysis (see above). At 250 °C, however, the phosphorus pentoxide became coated with carbonaceous material and the product comprised the starting material (82%) and a white solid which melted when warmed to room temperature to give a colourless liquid that rapidly became pink; the presence of an isocyanide in the pink liquid, indicated by its vile odour, was confirmed by i.r. spectroscopy (λ_{NC} 4.69 μm), which also detected the presence of pentafluoroaniline. Use of an alkali-washed (NaOH) Pyrex tube, in an attempt to restrain polymerization or resinification of the isocyanide on the hot acidic glass surface,¹² raised the consumption of pentafluoroformanilide to 85% and increased both the isocyanide content of the liquid

⁴ A. W. Hofmann, *Annalen*, 1867, 144, 114; 1868, 146, 107.

⁵ I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer, and K. Offermann, *Angew. Chem. Internat. Edn.*, 1965, 4, 472.

⁶ R. E. Banks, R. N. Haszeldine, and C. W. Stephens, *Tetrahedron Letters*, 1972, 3699.

⁷ B. G. Willoughby, Ph.D. Thesis, University of Manchester, 1971.

⁸ A. I. Vogel, 'A Text-book of Practical Organic Chemistry,' Longmans Green, London, 1948, p. 620.

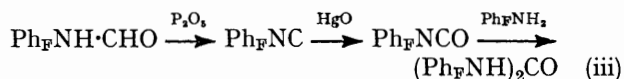
⁹ D. Samuel, B. Weinraub, and D. Ginsburg, *J. Org. Chem.*, 1956, 21, 376.

¹⁰ W. P. Weber and G. W. Gokel, *Tetrahedron Letters*, 1972, 1637.

¹¹ J. Burdon, J. Castaner, and J. C. Tatlow, *J. Chem. Soc.*, 1964, 5017; G. M. Brooke and R. J. D. Rutherford, *J. Chem. Soc. (C)*, 1967, 1189.

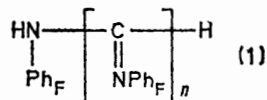
¹² F. Millich, *Chem. Rev.*, 1972, 72, 101.

product and its depth of colour. That pentafluorophenyl isocyanide was present received chemical confirmation when the gaseous pyrolysate was passed over mercury(II) oxide at 120 °C to give a mixture containing pentafluorophenyl isocyanate and *NN'*-bis(pentafluorophenyl)urea [reaction (iii)]. Passage of pentafluoro-



formanilide through an empty alkali-washed Pyrex tube at 250 °C caused no change, but contact with calcium oxide at that temperature gave an equimolar mixture of pentafluoroaniline and carbon monoxide (15% yield based on 45% recovery of the anilide); such decarbonylation accompanies the formation of indoles in the Madelung pyrolysis of amides derived from *o*-toluidine,¹³ but otherwise appears rare.

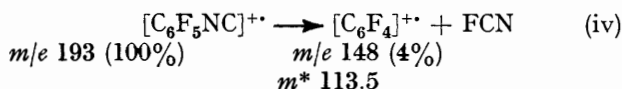
Nothing distilled from the pink liquid containing pentafluorophenyl isocyanide when it was stored at 22 °C *in vacuo* in a flask connected to a trap cooled to -196 °C, but the pink colour changed through red to dark brown during 24 h; this change, which was accompanied by steady loss in the intensity of the i.r. absorption caused by the isocyanide at 4.69 μm, was accelerated by heat or by addition of water. The exact cause of the pink colour was not determined, but its rapid development when the colourless pentafluoroformanilide dehydration product was warmed from solid CO₂ temperature to ambient temperature conforms with the spontaneous formation of coloured materials from other isocyanides.¹² After storage at room temperature for 4 weeks, the pink liquid had changed into a brown tar which, following removal of any volatile material at 100 °C *in vacuo*, possessed a mass spectrum with a top mass peak of *m/e* 955 and a recurring pattern of groups of peaks, corresponding peaks in adjacent groups being separated by *m/e* 193 (C₇F₅N); this pattern, together with the presence of saturated peaks at *m/e* 194 (C₇HF₅N⁺) and *m/e* 182 (C₆HF₅N⁺) and the appearance of i.r. absorptions at 3.1w,br (N-H str.), 3.35w (C-H str.), 5.9m,br (C=N str.), and 6–7s (C₆F₅) μm (chloroform solution) suggests the presence of polymeric material of type (1). A brown solid obtained later (see below) by allowing a mixture of pentafluorophenyl isocyanide and pentafluorophenyl cyanide to 'mature' at room temperature for 2 weeks possessed a similar i.r. spectrum and also gave correct analytical figures



(C₇H₂F₅N) for poly(pentafluorophenyl isocyanide). Poly(trifluoromethyl isocyanide)^{3b} and hydrocarbon polyisocyanides¹² are also thought to possess repeating units of the imine type.

¹³ W. Madelung, *Ber.*, 1912, **45**, 1128; F. T. Tyson, *J. Amer. Chem. Soc.*, 1941, **63**, 2024.

All efforts to isolate pentafluorophenyl isocyanide failed, including treatment of the pink liquid with bromine in an effort to produce the dibromide C₆F₅N:CB₂. More than twenty further pyrolysis experiments (250 °C; P₂O₅) under varied conditions showed that it was difficult to get reproducible results. A small amount (<1% yield) of a *ca.* 6:1 mixture of pentafluorophenyl isocyanide and pentafluorophenyl cyanide, analysed by ¹⁹F n.m.r. spectroscopy, was thus obtained. The u.v. spectrum of the 6:1 mixture contained a strong absorption near 270 nm, *i.e.* in the region characteristic of aryl isocyanides where marked interaction of the isocyano-group with the aromatic nucleus occurs,¹⁴ and the mass spectrum (after subtraction of peaks caused by pentafluoroaniline) was consistent with fragmentation of the molecular ion *via* α-scission and loss of FCN [see (iv)] (*cf.*¹⁵ loss of HCN from molecular ions in the spectra of hydrocarbon aryl isocyanides).



EXPERIMENTAL

I.r., u.v., n.m.r., and mass spectra were recorded on a Perkin-Elmer 257 or 621 spectrophotometer, a Unicam SP 700 spectrophotometer, a Perkin-Elmer R10 or Hitachi R-20A spectrometer (60 MHz for ¹H, and 56.46 MHz for ¹⁹F) or a Varian HA100 instrument (100 MHz for ¹H and 94.1 MHz for ¹⁹F), and an A.E.I. MS902 spectrometer (electron beam energy 70 eV), respectively.

Pentafluoroformanilide.—Pentafluoroaniline (40 g, 0.21 mol) in tetrahydrofuran (40 cm³) was added dropwise during 10 min to a stirred suspension of sodium hydride (5.0 g, 0.21 mol) in tetrahydrofuran (300 cm³) contained in a flask (1 l) cooled to *ca.* -20 °C (ice-salt) and fitted with a silica-gel guard tube. The mixture was stirred for 4 h at -15 to -20 °C, then treated with ethyl formate (16 g, 0.21 mol) in tetrahydrofuran (40 cm³) (the solution was added dropwise during 5 min), and allowed to warm to room temperature. The product was acidified (litmus) with glacial acetic acid, diluted with ether (300 cm³), then stirred for 2 h and finally filtered. The filtrate was distilled *in vacuo* and the solid brown residue crystallised from carbon tetrachloride; recrystallisation of the product from the same solvent provided 2',3',4',5',6'-pentafluoroformanilide (25.1 g, 0.12 mol, 55%) (Found: C, 39.8; H, 0.9; F, 44.5; N, 6.8. C₇H₂F₅NO requires C, 39.8; H, 0.9; F, 45.0; N, 6.6%) as white needles, m.p. (sealed tube) 100 °C.

Pentafluoroformanilide is a white solid that sublimes readily above 70 °C and exhibits polymorphism: crystals grown in solutions of the anilide in carbon tetrachloride or by sublimation and condensation of the vapour on a warm glass surface were needle-like (modification A) and, as a mull in Nujol or hexachlorobutadiene, possessed an i.r. spectrum which was similar to yet distinct from that of crystallites (modification B) obtained by cooling molten pentafluoroformanilide or by sublimation using a cold glass condenser. The i.r. spectrum of A showed absorptions

¹⁴ I. Ugi and R. Meyer, *Chem. Ber.*, 1960, **93**, 239.

¹⁵ B. Zeeh, *Org. Mass Spectrometry*, 1968, **1**, 315 (*Chem. Abs.*, 1968, **69**, 76 387).

at 3.12 μ (H-bonded N-H str.), 5.96 (C=O str.; this band showed characteristic 'Amide I' behaviour in that a marked shift to shorter wavelength accompanied by a significant increase in intensity occurred when solutions of A in chloroform or carbon tetrachloride were examined), 6.06 (C₆F₅), 6.45, 6.56 ('Amide II' band), and 6.68 μ m (C₆F₅), whereas the corresponding absorptions for B occurred at 3.05, 5.95, 6.06, 6.48, 6.54, and 6.68 μ m; solutions of A and B in chloroform or carbon tetrachloride gave identical spectra, dilute (0.5% w/v) solutions in the latter solvent exhibiting two sharp bands in the N-H str. region at 2.92 and 2.95 μ m, the latter being about two-thirds as intense as the former and assigned as the first overtone of the carbonyl absorption (*cf.* ref. 16), which appeared at 5.78 μ m. Recrystallisation of modification B from carbon tetrachloride gave modification A.

¹H N.m.r. spectra of solutions of pentafluoroformanilide in acetone or chloroform showed no evidence of the co-existence of *cis*- and *trans*-isomers arising from hindered rotation about the N-C(O) bond. In acetone solution (30% w/v) at 35 °C, the anilide gave a 60 MHz spectrum comprising two peaks of equal intensity at τ 0.9vbr (NH) and 1.53 (CH), and as the temperature was lowered the first of these moved to lower field (τ 0.0 at -80 °C) and sharpened considerably, presumably owing to more efficient quadrupole relaxation, but no splitting occurred. The 94.1 MHz ¹⁹F spectrum of pentafluoroformanilide in acetone (20% w/v) at 35 °C comprised three bands of relative intensities 2:1:2 at 68.4, 82.1, and 88.0 p.p.m. to high field of external trifluoroacetic acid, assigned to *ortho*-, *para*-, and *meta*-fluorines, respectively; the fine structure was only poorly resolved, but by lowering the temperature to -20 °C a value for one coupling constant ($|J_{3,4}|$ 21.9 Hz) was obtained. Comparison of these ¹⁹F chemical shift data with data for hexafluorobenzene (85.0 p.p.m. upfield from trifluoroacetic acid) and pentafluoroaniline [*ca.* 20% (w/v) solution in acetone; 87.2 (*o*-F), 91.0 (*m*-F), and 101.5 (*p*-F) p.p.m. (*cf.* ref. 17)] suggests that the NH-CHO group is mildly electron-withdrawing and that no significant electron release from nitrogen to the ring occurs. The u.v. spectrum of pentafluoroformanilide supports the conclusion that marked steric interactions exist between the NH-CHO group and the *ortho*-fluorines: in ethanol, the principal absorption of the anilide is less intense and occurs at slightly shorter wavelength [λ_{\max} 221–222 nm (ϵ 8 970)] than the corresponding absorption for pentafluoroaniline [λ_{\max} 224.5 (ϵ 13 950)] (*cf.* ref. 18).

The mass spectrum of pentafluoroformanilide shows major peaks at *m/e* 211 (*M*⁺, C₇H₂F₅NO⁺ 44%), 183 (C₆H₂F₅N⁺, 100), 155 (C₆F₅⁺, 19), 136 (C₅F₄⁺, 18), 117 (C₅F₃⁺, 12), 69 (CF₃⁺, 10), 29 (CHO⁺, 10), and 28 (CO⁺, 12); the appearance of a metastable peak at *m/e* 158.7 confirms that decarbonylation is the principal mode of fragmentation of the molecular ion.

Reactions of Pentafluoroformanilide.—(a) *Hydrolysis.* Pentafluoroformanilide (1.00 g, 4.74 mmol), heated under reflux with 0.5M-sulphuric acid (25 cm³) for 30 min, then rendered alkaline (2M-sodium hydroxide) gave, *via* extraction with ether, pentafluoroaniline (0.37 g, 2.01 mmol, 42%). Similarly, treatment of pentafluoroformanilide (1.00 g) with boiling 5M-sodium hydroxide (25 cm³) for 30 min gave 0.55 g (3.00 mmol, 63%) of pentafluoroaniline.

(b) *Pyrolysis.* Pentafluoroformanilide (1.0 g) was re-

covered quantitatively after being sublimed (45 min) through an evacuated silica tube (870 \times 16 mm) heated to 500 °C over 344 mm of its length.

Passage of pentafluoroformanilide vapour (2.0 g) during 60 min through a hot (250 °C) evacuated Pyrex tube (heated length 344 mm, diameter 15 mm) packed with Fenske single-turn glass helices (2.5 mm) resulted only in quantitative recovery.

(c) *With phosphoryl chloride.* Addition of pentafluoroformanilide (3.0 g, 15 mmol), to a solution of potassium (1.75 g, 0.045 g atom) in *t*-butyl alcohol (20 cm³), followed by addition of phosphoryl chloride (2.25 g, 15 mmol), and stirring and heating at 50 °C for 5 min gave only an unidentified hard brown solid.

(d) *With phosgene.* Phosgene (4.95 g, 50 mmol) was bubbled into a cold (0 °C) stirred mixture of pentafluoroformanilide (10.0 g, 47 mmol), triethylamine (12.0 g, 0.12 mmol), and methylene chloride (125 cm³) during 60 min. After being stirred at 0 °C for 60 min, the mixture was evaporated *in vacuo* to give a brown solid which was recrystallised from carbon tetrachloride to provide a mixture (3.2 g) of triethylamine hydrochloride (mainly) and pentafluoroformanilide, identified by i.r. spectroscopy. Evaporation of the mother liquor left an unidentified brown solid.

(e) *With phosphorus pentaoxide.* (i) *In untreated Pyrex.* Pentafluoroformanilide (2.0 g, 9.5 mmol) was packed into the sealed end of a Pyrex pyrolysis tube (900 \times 15 mm i.d.) and held in place with a small plug of glass wool. The central portion (450 mm) of the tube was half filled with phosphorus pentaoxide, and the tube was then placed in a horizontal furnace (heated length 344 mm) so that the sealed end protruded; the apparatus was evacuated continuously *via* three cold traps (-78, -196, and -196 °C) and the temperature of the furnace was raised to 250 °C; after 30 min the pyrolysis tube was pushed slowly into the furnace so that the pentafluoroformanilide sublimed into the zone containing hot phosphorus pentaoxide. After 30 min the products were pentafluoroformanilide (1.64 g, 82%), which collected near the entrance to the train of cold traps, and a white solid (at -78 °C) that changed into a pink liquid (0.1 g) when warmed to room temperature.

(ii) *In alkali-washed Pyrex.* Experiment (i), repeated using a new Pyrex tube which had been kept full of 10M-sodium hydroxide for 48 h, drained (30 min), dried in an oven at 80 °C, then flamed-out, gave pentafluoroformanilide (0.3 g, 15%), an unidentified black tar (*ca.* 0.4 g), and a pink liquid mixture (0.7 g) of pentafluorophenyl isocyanide and pentafluoroaniline. The colour of the pink liquid was noticeably deeper than in the experiment with the untreated Pyrex tube, and the i.r. absorption at 4.69 μ m was more intense.

(iii) *Followed by isocyanide 'trapping.'* Experiment (ii) was repeated with 2.0 g (9.5 mmol) of pentafluoroformanilide, but a Pyrex tube (650 \times 15 mm) containing yellow mercury(II) oxide (11 g, 51 mmol) heated to 120 °C by an auxiliary furnace was inserted between the main alkali-washed Pyrex pyrolysis tube containing phosphorus pentaoxide at 250 °C and the three cold traps. Silvery-grey streaks (presumably mercury) formed in the tube containing mercury(II) oxide, and a white solid condensed in the upper regions of the -78 °C trap; when the evacuated trap was raised so that only the lower half remained in the coolant, a small amount of the white solid was transferred

¹⁶ R. A. Nyquist, *Spectrochim. Acta*, 1963, **19**, 1595.

¹⁷ I. J. Lawrenson, *J. Chem. Soc.*, 1965, 1117.

¹⁸ J. G. Allen, J. Burdon, and J. C. Tatlow, *J. Chem. Soc.*, 1965, 6329.

to the colder section by sublimation, leaving behind *NN'*-bis(pentafluorophenyl)urea (0.03 g), m.p. 270 °C, identified by comparison of its i.r. spectrum with that of a sample (m.p. 269.5–270 °C) prepared by treatment of pentafluorophenyl isocyanate with pentafluoroaniline; the sublimate melted when warmed to room temperature to give a small volume of a pink liquid containing (by i.r. spectroscopy) pentafluorophenyl isocyanide, pentafluorophenyl isocyanate, and *NN'*-bis(pentafluorophenyl)urea.

Pyrolysis of 4.0 g (19 mmol) of pentafluoroformanilide over phosphorus pentoxide followed by passage of the product over mercury(II) oxide (22.0 g, 102 mmol), as above, gave *NN'*-bis(pentafluorophenyl)urea (0.05 g, 0.13 mmol), as white needles from toluene (Found: C, 39.8; H, 0.8; F, 48.5; N, 7.35%; M^+ , 392. Calc. for $C_{13}H_2F_{10}N_2O$: C, 39.8; H, 0.5; F, 48.5; N, 7.1%; M , 392).

(f) *With calcium oxide.* Pentafluoroformanilide vapour (2.0 g, 9.5 mmol), passed during 30 min through a hot (250 °C), evacuated Pyrex tube (heated section 344×15 mm) containing a bed of calcium oxide (10.0 g, 180 mmol), as described in experiment (e) (i) except that the apparatus was isolated from the pumping system during the pyrolysis, gave carbon monoxide (0.62 mmol, 7%), pentafluoroaniline (0.12 g, 0.66 mmol, 7%) (recovered from the -78 °C trap), and pentafluoroformanilide (0.89 g, 45%).

(g) *With sodium hydroxide.* Pentafluoroformanilide vapour (2.0 g) was passed during 30 min through an alkali-washed [see experiment (e) (ii)] Pyrex tube heated to 250 °C and evacuated prior to pyrolysis. No material condensed in the cold traps, no non-condensable material was formed, and 1.93 g (96%) of pentafluoroformanilide was recovered from the cool exit of the pyrolysis tube. The amount of sodium hydroxide (*ca.* 0.15 g) in the heated section (344×15 mm) of the Pyrex pyrolysis tube (900×15 mm) used was estimated by weighing a smaller tube (165×15 mm) before and after treatment with aqueous sodium hydroxide as described in experiment (e) (ii).

Characterisation of Pentafluorophenyl Isocyanide.—(a) *By mass spectrometry.* Pentafluoroformanilide vapour (2.0 g, 9.5 mmol) was passed over phosphorus pentoxide (5 g) (introduced using dry box techniques) at 250 °C in an alkali-washed Pyrex tube during 60 min; prior to the pyrolysis the apparatus was evacuated then isolated from the pump. A non-condensable product was collected by adsorption on activated charcoal at -196 °C and shown by i.r. analysis and mass spectrometry to be carbon monoxide (5.2 mmol); the only other product was a white solid (0.15 g) that melted to a pink liquid when the cold trap (-78 °C) was warmed to 20 °C. The pink, foul-smelling liquid was shown by i.r. spectroscopy and mass spectrometry (source temperature 200 °C) to contain only pentafluoroaniline and pentafluorophenyl isocyanide; the mass

spectrum of the latter, deduced through comparison of the spectrum of the mixture with that of pentafluoroaniline measured under identical conditions, showed *m/e* 193 [$C_7F_5N^+$, 96% (relative to the base peak in the spectrum of the mixture, which corresponded to pentafluoroaniline radical cation)], 174 ($C_7F_4N^+$, 2), 167 ($C_6F_5^+$, 1), 163 (2), 156 (1), 148 ($C_6F_4^+$, 4), 143 ($C_6F_3N^+$, 3), 136 ($C_5F_4^+$, 1), 125 (2), 124 ($C_6F_2N^+$, 16), 117 ($C_5F_3^+$, 4), 113 (1), 105 (C_6FN^+ , $C_4F_3^+$, 2), 100 ($C_2F_4^+$, 2), 98 ($C_5F_2^+$, 2), 96.5 ($C_7F_5N^{++}$, 4), 93 (C_5FN^+ , $C_3F_3^+$, 8), 86 (C_6N^+ , $C_4F_2^+$, 1), 85 (1), 82 (1), 81 (C_4FN^+ , $C_2F_3^+$, 1), 79 (C_5F^+ , 2), 76 (CF_4^+ , 1), 74 (C_5N^+ , $C_3F_2^+$, 2), 69 (CF_3^+ , 3), 62 (C_4N^+ , $C_2F_2^+$, 1), 45 (CFN^+ , 1), and 31 (CF^+ , 13), and an ($M + 1$) peak (8%) at *m/e* 194.

(b) *By u.v. spectroscopy.* The above experiment was repeated and a solution of the pink liquid from the -78 °C trap in hexane was shown to possess a u.v. spectrum similar to that of pentafluoroaniline except for a strong absorption near 270 nm.

(c) *By n.m.r. spectroscopy.* Pentafluoroformanilide (2.0 g) was pyrolysed *in vacuo* at 250 °C during 41 min using a new, untreated Pyrex tube containing 15 g of phosphorus pentoxide. Carbon monoxide (4.6 mmol) and a red liquid (0.05 g; condensed in a -78 °C trap as a white solid) were obtained; the latter was shown to be a *ca.* 6 : 1 mixture of pentafluorophenyl isocyanide and pentafluorophenyl cyanide by i.r. and n.m.r. spectroscopy. The ^{19}F n.m.r. spectrum of a *ca.* 5% (v/v) solution in acetone of the red liquid showed absorptions to high field of external trifluoroacetic acid at 57.7, 67.6, and 83.2 p.p.m., corresponding to those shown by an authentic sample of pentafluorophenyl cyanide dissolved in acetone, and complex bands at 67.8, 75.4, and 85.0 p.p.m. assigned, respectively, to the *ortho*-, *para*-, and *meta*-fluorines of pentafluorophenyl isocyanide (analysed as an AA'PXX' spectrum; $|J_{2,4}|$ 2.3, $|J_{3,4}|$ 20.3, $|J_{2,6}|$ 7.1, $|J_{3,5}|$ 0.9, $J_{2,3} \pm 20.3$, $J_{2,5} \mp 6.4$ Hz).

Poly(pentafluorophenyl isocyanide).—The acetone solution used in the ^{19}F n.m.r. investigation was stored at room temperature for 14 days, after which the characteristic isocyanide absorption at 4.69 μm in its i.r. spectrum had disappeared. Evaporation at 20 °C *in vacuo* gave a brown solid [Found: C, 43.5; H, 0.3; F, 48.6; N, 7.6. Calc. for $(C_6F_5NC)_n$: C, 43.5; H, 0.0; F, 49.2; N, 7.3%], the i.r. spectrum of which (film deposited by evaporation of a solution in diethyl ether) contained absorptions characteristic of C:N (5.9 μm) and pentafluorophenyl groups.

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