Studies in Azide Chemistry. Part V.[1] Synthesis of 4-Azido-2,3,5,6-tetrafluoro-, 4-Azido-3-chloro-2,5,6-trifluoro-, and 4-Azido-3,5-dichloro-2,6-difluoro-pyridine, and Some Thermal Reactions of the Tetrafluoro-compound

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4-Azido-2,3,5,6-tetrafluoropyridine can be prepared by nitrosation of 2,3,5,6-tetrafluoro-4-hydrazinopyridine or, preferably, treatment of pentafluoropyridine with sodium azide in acetonitrile, a reagent that converts 3-chloro-2,4,5,6-tetrafluoro- and 3,5-dichloro-2,4,6-trifluoro-pyridine into 4-azido-3-chloro-2,5,6-trifluoro- and 4-azido-3,5-dichloro-2,6-difluoro-pyridine, respectively. 4-Azido-2,3,5,6-tetrafluoropyridine decomposes smoothly into nitrogen and an intractable solid at temperatures above *ca.* 130 °C, undergoes the Staudinger reaction with triphenylphosphine at room temperature, reacts with dimethyl sulphoxide at elevated temperatures to give a sulphoximide, partakes in 1,3-dipolar cycloaddition reactions with benzyne, diphenylacetylene, phenylacetylene, cyclopentadiene dimer, and norbornene, yields 4-anilino-2,3,5,6-tetrafluoropyridine with benzene at 175 °C, and reacts with cyclohexane to give the C–H ' insertion ' product 4-(cyclohexylamino)-2,3,5,6-tetrafluoropyridine and 4-amino-2,3,5,6-tetrafluoropyridine. Thermal decomposition of the azide in a mixture of cyclo-hexane, -heptane, and -octane reveals that C–H ' insertion ' is encouraged by increase in ring size, and thermolysis experiments with *cis*- and *trans*-1,2-dimethylcyclohexane show that this type of reaction lacks stereospecificity. The results of reactions between the azide and *trans*-4-methylpent-2-ene at elevated temperatures indicate that 1,3-dipolar cycloaddition occurs before nitrene generation can be achieved. Authentic samples of the new aminopyridines [$PhNHpy_F$, cyclo-C_nH_{2n-1}·$NHpy_F$ (*n* = 6, 7, or 8), *cis*- and *trans*-cyclo-1,2-$Me_2C_6H_9$·$NHpy_F$, and *cis*- and *trans*-Pr^iCH·CHMe·Npy_F (py_F = 2,3,5,6-tetrafluoro-4-pyridyl)] encountered in this work can be obtained *via* nucleophilic attack by the appropriate amines on pentafluoropyridine.

THE literature contained little information on aromatic azides of the fluorocarbon class when we embarked on the work now reported: azidopentafluorobenzene and several related carbocyclic polyfluoroaryl azides had been prepared from the corresponding hydrazino-compounds,[2,3] and thermal decomposition of azidopentafluorobenzene into nitrogen and an unidentified brown solid had been shown to occur smoothly within the temperature range 80—120 °C.[2] Since we prepared the three title compounds of this paper, details have been published of the conversion of 3,5-dichloro-2,4,6-trifluoropyridine into 4-azido-3,5-dichloro-2,6-difluoropyridine,[4] hexafluorobenzene into azidopentafluoro- and 1,4-diazidotetrafluorobenzene,[5] chloropentafluorobenzene into 1-azido-4-chlorotetrafluorobenzene,[5] octafluorotoluene into 1-azido-4-trifluoromethyltetrafluorobenzene,[5] and pentafluorobenzonitrile into 1-azido-4-cyanotetrafluorobenzene [6] *via* S_NAr reactions involving sodium azide in dimethylformamide or acetone. Azide ion attack on 2,3,4,6-tetrafluoropyridine,[7] perfluoro-(4-isopropylpyridine),[8] tetrafluoropyrimidine,[9] and perfluoro-3,3'-bipyridyl [7] has also been employed recently to obtain 4-azido-2,3,6-trifluoropyridine, perfluoro-(2-azido-4-isopropylpyridine) and perfluoro-(2,6-diazido-4-isopropylpyridine), 4,6-diazido-2,5-difluoropyrimidine, and perfluoro-4-azido-3,3'-bipyridyl, respectively.

Initially, 4-azido-2,3,5,6-tetrafluoropyridine was obtained (44% yield) by nitrosation of 2,3,5,6-tetrafluoro-4-hydrazinopyridine, *i.e.* the type of reaction used earlier [2] to procure the first pure sample of azidopentafluorobenzene. Treatment of pentafluoropyridine with sodium azide in acetonitrile at room temperature is a superior method; nucleophilic displacement of fluorine apparently occurs exclusively from the 4-position, as expected,[10] and the azido-compound can be isolated in at least 69% yield. Application of the latter type of reaction to 3-chloro-2,4,5,6-tetrafluoro- and 3,5-dichloro-2,4,6-trifluoro-pyridine provides 4-azido-3-chloro-2,5,6-trifluoro- and 4-azido-3,5-dichloro-2,6-difluoro-pyridine (76 and 77%), respectively.

4-Azidotetrafluoropyridine is a colourless, mobile liquid, b.p. 53 °C at 7·5 mmHg, which slowly turns yellow when stored at room temperature. It does not explode when struck with a hammer, and visibly evolves nitrogen only when heated above 130 °C; at temperatures in the range 160—175 °C, it readily decomposes into nitrogen and an intractable brown solid, m.p. >360 °C. The

[1] Part IV, R. E. Banks and M. J. McGlinchey, *J. Chem. Soc.* (*C*), 1971, 3971.

[2] J. M. Birchall, R. N. Haszeldine, and A. R. Parkinson, *J. Chem. Soc.*, 1962, 4966.

[3] R. N. Haszeldine, A. R. Parkinson, and J. M. Birchall, U.S.P. 3,238,230/1966. [Note, however, that except for the case of 4-azidopentafluorobenzene, no data (yield, physical constants, elemental composition, spectroscopic properties) relating to the azides claimed are quoted. Similarly, no details are recorded for the photochemical and 1,3-dipolar cycloaddition reactions claimed for some of the polyfluoroazidoarenes.]

[4] C. D. S. Tomlin, J. W. Slater, and D. Hartley, B.P. 1,161,492/1969.

[5] A. V. Kashkin, Yu. L. Bakhmutov, and N. N. Marchenko, *Zhur. vsesoyuz. Khim. Obshchest.*, 1970, **15**, 591 (*Chem. Abs.*, 1971, **74**, 12,729k). A single attempt by a member of our group (A. Prakash) to carry out this preparation of 4-azidopentafluorobenzene ended when a violent explosion occurred during distillation of the product.

[6] J. M. Birchall, R. N. Haszeldine, and M. E. Jones, *J. Chem. Soc.* (*C*), 1971, 1343.

[7] R. E. Banks and G. R. Sparkes, unpublished results.

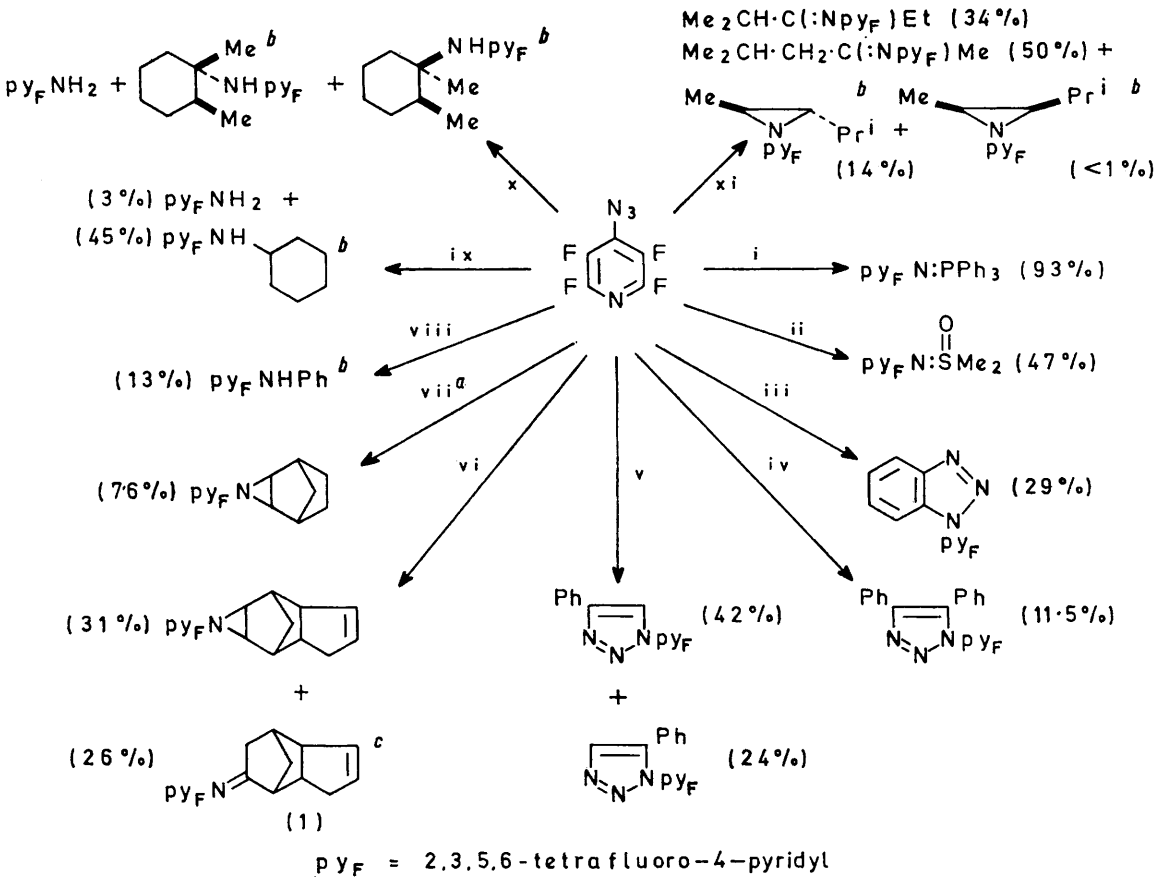
[8] R. E. Banks and A. Prakash, in preparation.

[9] R. E. Banks, R. N. Haszeldine, and R. S. Jacques, unpublished results.

[10] R. E. Banks, ' Fluorocarbons and their Derivatives,' 2nd edn., Macdonald, London, 1970.

thermal reactions of 4-azidotetrafluoropyridine now reported are summarised in Scheme 1; the behaviour of the azide [and of the related compounds azidopentafluorobenzene and perfluoro-(2-azido-4-isopropylpyridine)] when subjected to flow pyrolysis is being investigated.[11]

Not unexpectedly,[12] 4-azidotetrafluoropyridine readily undergoes a Staudinger reaction with triphenylphosphine, partakes in 1,3-dipolar cycloadditions with benzyne, diphenylacetylene, and phenylacetylene, and attacks tricyclo[5,2,1,$0^{2,6}$]dec-3- and/or 4-en-8-one (from cyclopentadiene dimer) or bicyclo[2,2,1]heptan-2-one (from norbornene); these products are believed to be artefacts, produced by hydrolysis of the imines (1) and (2), respectively, during work-up. The failure to obtain Δ^2-1,2,3-triazolines from reactions between 4-azidotetrafluoropyridine and cyclopentadiene dimer or norbornene at room temperature supports the contention that electron-withdrawing substituents at N-1 in such heterocycles promote thermal instability.[13]



SCHEME 1 Some thermal reactions of 4-azido-2,3,5,6-tetrafluoropyridine

Reagents: i, Ph_3P, Et_2O, 20 °C; ii, Me_2SO, 160 °C; iii, *o*-$H_2N{\cdot}C_6H_4{\cdot}CO_2H$, $Bu^nO{\cdot}NO$, CH_2Cl_2, 40 °C; iv, PhC:CPh, CCl_4, 77 °C; v, PhC:CH, CCl_4, 77 °C; vi, *endo*-cyclopentadiene dimer, light petroleum, 20 °C; vii, norbornene, light petroleum, 20 °C; viii, C_6H_6, 175 °C; ix, cyclo-C_6H_{12}, 170 °C; x, *cis*- or *trans*-1,2-dimethylcyclohexane, 170 °C; xi, *trans*-MeCH:CH·$CHMe_2$, 175 °C.

the strained olefinic bonds in *endo*-cyclopentadiene dimer and norbornene under mild conditions. The reactions involving the last two substrates, which presumably occur *via* the formation (by 1,3-dipolar cycloaddition processes) and subsequent rapid thermal decomposition of Δ^2-1,2,3-triazolines, also gave 4-amino-2,3,5,6-tetrafluoropyridine and material believed to be

SS-Dimethyl-*N*-(tetrafluoro-4-pyridyl)sulphoximide is formed when a solution of 4-azidotetrafluoropyridine in dimethyl sulphoxide is heated, the reaction occurring much more readily at 160 than at 100 °C. This suggests * that thermolysis of the azide is a convenient source of tetrafluoro-4-pyridylnitrene, a notion supported [12,15] by the formation of 4-cyclohexylamino- and

* Sulphoxides are among the best reagents yet discovered for intercepting nitrenes.[14]

[11] R. E. Banks and A. Prakash, investigations in progress.

[12] For recent reviews of the chemistry of organic azides see 'The Chemistry of the Azido Group,' ed. S. Patai, Wiley-Interscience, London, 1971, and G. L'abbe, *Chem. Rev.*, 1969, **69**, 345.

[13] For a detailed review of triazoline decomposition see P. Scheiner in 'Selective Organic Transformations,' ed. B. S. Thyagarajan, Wiley-Interscience, New York, 1970, vol. 1, p. 327.

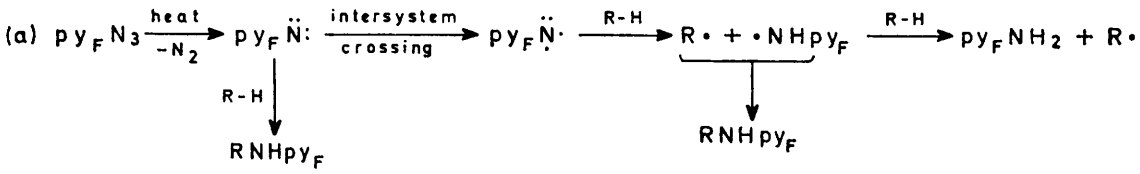
[14] D. J. Anderson, D. C. Horwell, E. Stanton, T. L. Gilchrist, and C. W. Rees, *J.C.S. Perkin I*, 1972, 1317.

[15] 'Nitrenes,' ed. W. Lwowski, Wiley-Interscience, New York, 1970.

4-anilino-tetrafluoropyridine when 4-azidotetrafluoropyridine is heated at 170—175 °C in the presence of cyclohexane and benzene, respectively. Mechanistically, formation of the anilino-derivative, which is accompanied by black ' polymeric ' material, seems best ascribed to attack on the aromatic substrate by singlet tetrafluoro-4-pyridylnitrene (presumably a highly electrophilic species relative to singlet phenylnitrene [16]); the C–H ' insertion ' with cyclohexane, however, which yields 4-aminotetrafluoropyridine and ' polymeric ' material as well as 4-(cyclohexylamino)tetrafluoropyridine, could involve singlet or triplet tetrafluoro-4-pyridylnitrene, or both [see Scheme 2(a)].

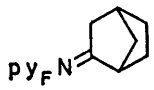
A technique used by Anastassiou and Simmons [17] in their work on cyanonitrene was employed to throw some light on the cyclohexane–4-azidotetrafluoropyridine reaction. Dilute solutions of the azido-compound in *cis*- and *trans*-1,2-dimethylcyclohexane were heated at 175 and 170 °C, respectively; ' polymer ' formation, production of 4-aminotetrafluoropyridine, and C–H ' insertion ' occurred, the last taking place preferentially and non-stereospecifically at the tertiary C–H bonds. Thus, *cis*-1,2-dimethylcyclohexane gave a *ca.* 1 : 2 mixture (42% yield) of the two isomeric 1,2-dimethyl-1-(tetrafluoro-4-pyridylamino)cyclohexanes (designated *A* and *B*, respectively, since the absolute stereochemistry of each is unknown) and the *trans*-substrate a *ca.* 2 : 1 mixture (53%) of *A* and *B*. If we assume that a nitrene mechanism is operative, this result clearly implicates a triplet species. When 4-azidotetrafluoropyridine was heated at 175 °C in the presence of a large excess of an equimolar mixture of cyclo-hexane, -heptane, and -octane, the expected C–H ' insertion ' products (total yield 79%) were obtained in a molar ratio of *ca.* 3 : 6 : 10; this low level of discrimination by the presumed tetrafluoro-4-pyridylnitrene for the methylene groups of the three cycloalkanes [affinity per CH_2 group = *ca.* 1·0(C-6) : 1·7(C-7) : 2·5(C-8)]militates [17] against the hydride abstraction process shown in Scheme 2(b), which would be expected to result in non-stereospecific ' insertion ' into the tertiary C–H bonds of the dimethylcyclohexanes.

An attempt to obtain information about the thermolysis of 4-azidotetrafluoropyridine by means of a nitrene trapping experiment involving *trans*-4-methylpent-2-ene was foiled by the apparent occurrence of 1,3-dipolar cycloaddition before the decomposition temperature of the azide was reached. Thus, with the exception of the *cis*-aziridine, the products observed after the reactants had been heated to 175 °C and kept at that temperature for 6 h (see Scheme 1) were obtained in almost identical yields from a reaction carried out at 65 °C for 8 h. From this, and the failure of the *cis*-aziridine to isomerise into imine material when heated at 170 °C for 5 h, it is assumed that the imines and most, if not all, of the aziridine product arose *via* fragmentation [13] of two isomeric Δ^2-1,2,3-triazolines produced by attack of undissociated 4-azidotetrafluoropyridine on the olefinic trap.



SCHEME 2 (*Cf.* ref. 17)

[a] The imine (2) is believed to be formed also (see text).



(2)

[b] Authentic samples of these new compounds were prepared from pentafluoropyridine and the appropriate amines (see Experimental section). [c] And/or the 9-(tetrafluoro-4-pyridylimino)-isomer.

EXPERIMENTAL

I.r., n.m.r. (shifts to high field designated positive), and mass spectroscopic analyses, respectively, were carried out with Perkin-Elmer spectrophotometers models 137 and 257 (absorption data quoted were obtained with the latter), a Perkin-Elmer R10 (^{19}F at 56·46, ^{1}H at 60 MHz) or Varian HA-100 (^{19}F at 94·10, ^{1}H at 100 MHz) instrument, and a G.E.C.-A.E.I. MS902 spectrometer (electron beam energy 70 eV). I.r. data for compounds marked with an asterisk are available in Supplementary Publications No. SUP 20521 (7 pp., 1 microfiche).*

Pentafluoro-, 3-chloro-2,4,5,6-tetrafluoro-, and 3,5-dichloro-2,4,6-trifluoropyridine were prepared by heating pentachloropyridine with potassium fluoride.[18] 2,3,5,6-Tetrafluoro-4-hydrazinopyridine was obtained by treating pentafluoropyridine with hydrazine hydrate.[19] To mini-

* For details of Supplementary Publications see *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (Notice to Authors No. 7).

[16] R. A. Abramovitch and E. F. V. Scriven, *Chem. Comm.*, 1970, 787; see also R. A. Abramovitch, S. R. Challand, and E. F. V. Scriven, *J. Amer. Chem. Soc.*, 1972, **94**, 1374.

[17] A. G. Anastassiou and H. E. Simmons, *J. Amer. Chem. Soc.*, 1967, **89**, 3177; A. G. Anastassiou, *ibid.*, p. 3184.

[18] R. E. Banks, R. N. Haszeldine, J. V. Latham, and I. M. Young, *J. Chem. Soc.*, 1965, 594; R. E. Banks, D. S. Field, and R. N. Haszeldine, *J. Chem. Soc.* (*C*), 1967, 1822.

[19] R. E. Banks, J. E. Burgess, W. M. Cheng, and R. N. Haszeldine, *J. Chem. Soc.*, 1965, 575.

mise possible explosion damage, the azidopyridines were usually prepared and manipulated on <10 g scale (often much less); prior to use, the azides were stored in stoppered Pyrex tubes in a compartmentalised steel box fitted with a perforated lid, and all reactions, distillations, *etc.* were conducted behind stout blast screens.

4-Azido-2,3,5,6-tetrafluoropyridine.—(a) *From 2,3,5,6-tetrafluoro-4-hydrazinopyridine.* The hydrazine (4·0 g, 22 mmol) in 5M-hydrochloric acid (60 ml) was cooled to 0—5 °C and mixed with ether (10 ml). Sodium nitrite (1·6 g, 23 mmol) in water (6 ml) was added slowly to the vigorously stirred mixture, which was kept at *ca.* 0 °C for 1 h then extracted with ether (5 × 20 ml). The extract was dried ($MgSO_4$) and distilled at reduced pressure to give *4-azido-2,3,5,6-tetrafluoropyridine* * (1·84 g, 9·58 mmol, 44%) [Found: C, 31·4; N, 29·3%; *M* (mass spec.), 192. $C_5F_4N_4$ requires C, 31·2; N, 29·2%; *M*, 192], b.p. 50—52 °C at 7·5 mmHg, $\lambda_{max.}$ (film) 4·51m-w, 4·59m, and 4·68s (t; N_3 asym. str.) μm, δ_F (ext. $CF_3{\cdot}CO_2H$) +14·3vbr (2-, 6-F) and +76·5 (3-, 5-F) p.p.m. (rel. int. 1 : 1), *m/e* 192 [$C_5F_4N_4^{+\bullet}$ ($M^{+\bullet}$), 94%], 164 [$C_5F_4N_2^{+\bullet}$ ($M^{+\bullet} - N_2$), 49%], 119 [$C_4F_3N^{+\bullet}$, 100%; *m** 86·3 ($C_5F_4N_2^{+\bullet} \longrightarrow C_4F_3N^{+\bullet} + FCN$)], and 28 ($N_2^{+\bullet}$, 31%).

(b) *From pentafluoropyridine.* Sodium azide (5·8 g, 89 mmol) was added slowly to a vigorously stirred solution of pentafluoropyridine (15·0 g, 88·8 mmol) in dry acetonitrile (100 ml) at room temperature. The mixture was stirred for 24 h then poured into water (1500 ml). The aqueous mixture was extracted with ether (3 × 200 ml), and the extract was dried ($MgSO_4$) then evaporated at reduced pressure and room temperature. Vacuum distillation of the residual yellow oil gave 4-azido-2,3,5,6-tetrafluoropyridine (11·7 g, 60·9 mmol, 69%), b.p. 53 °C at 7·5 mmHg, identified by its i.r. spectrum.

Similar reactions carried out at −23 and 21 °C but with dimethylformamide as solvent instead of acetonitrile gave 4-azidotetrafluoropyridine in 59 and 51% yield, respectively.

4-Azido-3-chloro-2,5,6-trifluoropyridine.—By use of the technique employed to convert pentafluoropyridine into 4-azidotetrafluoropyridine, 3-chloro-2,4,5,6-tetrafluoropyridine (8·0 g, 43 mmol) was treated with sodium azide (2·8 g, 43 mmol) in dry acetonitrile (100 ml) at room temperature to give *4-azido-3-chloro-2,5,6-trifluoropyridine* * (6·85 g, 32·8 mmol, 76%) (Found: C, 29·1; N, 26·6. $C_5ClF_3N_4$ requires C, 28·8; N, 26·9%), b.p. 61 °C at 3 mmHg, $\lambda_{max.}$ (film) 4·46w, 4·59m, and 4·71s (triplet; N_3 asym, str.) μm, δ_F (ext. $CF_3{\cdot}CO_2H$) −4·0br (2-F, d of d), +12·3br (6-F, d of d), and +78·1 (5-F, d of d) p.p.m. (rel. int. 1 : 1 : 1), *m/e* 210 ($C_5{}^{37}ClF_3N_4^{+\bullet}$, 31%) and 208 ($C_5{}^{35}ClF_3N_4^{+\bullet}$, 100%).

4-Azido-3,5-dichloro-2,5,6-trifluoropyridine.—By use of the techniques employed to prepare and isolate 4-azidotetrafluoropyridine, 3,5-dichloro-2,4,6-trifluoropyridine (8·08 g, 40·0 mmol) was treated with sodium azide (2·6 g, 40 mmol) in dry acetonitrile to give 4-azido-3,5-dichloro-2,6-difluoropyridine * (6·77 g, 30·9 mmol, 77%) (Found: C, 26·9; N, 24·8. Calc. for $C_5Cl_2F_2N_4$: C, 26·6; N, 24·9%), isolated by distillation as a colourless liquid, b.p. 74—75 °C at 2 mmHg, which solidified on storage at room temperature to pale green crystals, m.p. 30—32 °C (lit.,[4] 30·5—32·5 °C), $\lambda_{max.}$ (melt) 4·50w (sh), 4·55m, and 4·76s (d; N_3 asym. str.) μm, δ_F (ext. $CF_3{\cdot}CO_2H$; 44% w/w soln. in Me_2CO) −4·58 (2-, 6-F; s) p.p.m., the mass spectrum of which showed *M*, *M* + 2, and *M* + 4 peaks [58, 38, and 6%; base peak *m/e* 161 ($C_5{}^{35}ClF_2N_2^+$, 100%)].

Reactions of 4-Azido-2,3,5,6-tetrafluoropyridine.—(a) *With triphenylphosphine.* A solution of triphenylphosphine (2·78 g, 10·6 mmol) in ether (20 ml) was added dropwise to a solution of 4-azidotetrafluoropyridine (2·0 g, 10·4 mmol) in ether (10 ml). The mixture turned dark yellow and evolution of a gas (presumed to be nitrogen) commenced at once. The mixture was heated under reflux for 4 h, then cooled, and the white crystals deposited were recrystallised from ether to provide *triphenyl-(2,3,5,6-tetrafluoro-4-pyridylimino)phosphorane* (4·10 g, 9·6 mmol, 93%) [Found: C, 64·6; H, 3·6; N, 6·7%; *M* (mass spec.), 426. $C_{23}H_{15}F_4N_2P$ requires C, 64·8; H, 3·5; N, 6·6%; *M*, 426] as white needles, m.p. 166·5—167·5 °C, δ_F (ext. $CF_3{\cdot}CO_2H$; 28% w/w soln. in Me_2CO) +20·8 (2-, 6-F) and +79·2 (3-, 5-F) p.p.m. (rel. int. 1 : 1), δ_H (ext. benzene) −0·57 p.p.m.

(b) *With dimethyl sulphoxide.* 4-Azidotetrafluoropyridine (2·47 g, 12·9 mmol) was heated with dimethyl sulphoxide (35 ml) at 160 °C until 12·9 mmol of nitrogen had been evolved (<6 h). The brown liquid product was poured into water (300 ml), and the aqueous mixture was extracted with ether (4 × 100 ml). The extract was washed with water (3 × 50 ml), dried ($MgSO_4$), and evaporated at the pump; the brown residue (1·9 g) crystallised from ethanol to give pale yellow platelets of *SS-dimethyl-N-(2,3,5,6-tetrafluoro-4-pyridyl)sulphoximide* (1·45 g, 5·99 mmol, 47%) [Found: C, 34·6; H, 2·7; N, 11·7%; *M* (mass spec.), 242. $C_7H_6F_4N_2OS$ requires C, 34·7; H, 2·5; N, 11·6%; *M*, 242], m.p. 103—105 °C, $\lambda_{max.}$ (mull) 8·14, 8·19 (d; S=O str.), and 8·66 (S=N str.) [20] μm, δ_F (ext. $CF_3{\cdot}CO_2H$; saturated soln. in $Cl_3C{\cdot}CN$) +15·7 (2-, 6-F) and +74·2 (3-, 5-F) p.p.m. (rel. int. 1 : 1), δ_H (ext. benzene) +3·26 (s, Me) p.p.m., *m/e* 242 [$C_7H_6F_4N_2OS^{+\bullet}$ ($M^{+\bullet}$), 100%], 227 ($C_6H_3F_4N_2OS^+$, 40%), 179 ($C_6H_3F_4N_2^+$, 40%), and 78 ($C_2H_6OS^+$, 42%); *m** 213 [$M^{+\bullet} \longrightarrow C_6H_3F_4N_2OS^+ + CH_3{\cdot}$ (242 ⟶ 227)] and 141 [$C_6H_3F_4N_2OS^+ \longrightarrow C_6H_3F_4N_2^+ + SO$ (227 ⟶ 179)].

Treatment of 4-azidotetrafluoropyridine (1·0 g) with an excess of dimethyl sulphoxide (15 ml) at 100 °C for 8 days gave *SS*-dimethyl-*N*-(tetrafluoro-4-pyridyl)sulphoximide in only 10% yield, together with unchanged azido-compound.

(c) *With benzyne.* Anthranilic acid (2·16 g, 15·8 mmol) in acetone (20 ml) was added dropwise to boiling methylene chloride (60 ml) containing n-butyl nitrite (1·70 g, 16·5 mmol) and 4-azidotetrafluoropyridine (3·0 g, 15·6 mmol). Methylene chloride was removed from the product at the pump, and the brown gummy residue was taken up in methylated spirit. The alcoholic solution was evaporated on a steam-bath until it deposited crystals when cooled. Recrystallisation of these from methylated spirit (twice) gave *1-(2,3,5,6-tetrafluoro-4-pyridyl)benzotriazole* (1·2 g, 4·5 mmol, 29%) [Found: C, 49·5; H, 1·6; N, 21·2%; *M* (mass spec.), 268. $C_{11}H_4F_4N_4$ requires C, 49·3; H, 1·5; N, 20·9%; *M*, 268] as white needles, m.p. 139—140 °C, δ_F (ext. $CF_3{\cdot}CO_2H$; 24% w/w soln. in hexamethylphosphoramide) +11·4 (2-, 6-F) and +68·5 (3-, 5-F) p.p.m. (rel. int. 1 : 1), δ_H (ext. benzene) −1·1 (complex; 5-, 6-H) and −1·6 (complex; 4-, 7-H) p.p.m. (rel. int. 1 : 1).

(d) *With diphenylacetylene.* A solution of 4-azidotetrafluoropyridine (2·16 g, 11·3 mmol) and diphenylacetylene (2·00 g, 11·2 mmol) in carbon tetrachloride (20 ml) was heated under reflux for 20 h. Removal of the carbon tetrachloride by distillation gave a yellow oil which, when cooled, deposited white crystals; these were fractionally crystallised from methylated spirit, to give diphenylacetylene (0·98 g,

[20] *Cf.* L. J. Bellamy, ' Advances in Infrared Group Frequencies,' Methuen, London, 1968, p. 193; D. T. Sauer, and J. M. Shreeve, *Inorg. Chem.*, 1972, **11**, 238.

49% recovery), identified by its i.r. spectrum, and *4,5-diphenyl-1-(2,3,5,6-tetrafluoro-4-pyridyl)-1,2,3-triazole* (0·49 g, 1·3 mmol, 11·5%) (Found: C, 61·7; H, 3·0; N, 14·9. $C_{19}H_{10}F_4N_4$ requires C, 61·6; H, 2·7; N, 15·1%), m.p. 202—203 °C, δ_F (ext. $CF_3{\cdot}CO_2H$; saturated soln. in hexamethylphosphoramide) +10·6 (2-, 6-F) and +67·6 (3-, 5-F) p.p.m. (rel. int. 1 : 1), δ_H (ext. benzene) −0·96br (s, Ph) p.p.m.

(e) *With phenylacetylene.* A solution of 4-azidotetrafluoropyridine (3·0 g, 15·6 mmol) and phenylacetylene (2·45 g, 24 mmol) in carbon tetrachloride (20 ml) was heated under reflux for 3 h. White crystals which appeared when the solution was cooled were filtered off and the filtrate was heated under reflux for 10 h, then cooled to yield pale yellow crystals. These were filtered off, and the filtrate was heated under reflux for 3 h, then cooled to provide more yellow crystals. Finally, the remaining carbon tetrachloride solution was evaporated to give a solid residue. The first three crops of crystalline material were shown by t.l.c. to be identical, so they were combined (1·74 g) and recrystallised from ethanol to give *4-phenyl-1-(2,3,5,6-tetrafluoro-4-pyridyl)-1,2,3-triazole* (1·6 g, 5·4 mmol, 35%) (Found: C, 52·9; H, 2·0; N, 19·3. $C_{13}H_6F_4N_4$ requires C, 53·1; H, 2·0; N, 19·1%) as white needles, m.p. 157—158 °C, δ_F (ext. $CF_3{\cdot}CO_2H$; saturated soln. in Me_2CO) +12·9 (2-, 6-F) and +71·4 (3-, 5-F) p.p.m. (rel. int. 1 : 1), δ_H (ext. benzene) −0·42 (complex; *m*-, *p*-H), −0·96 (complex; *o*-H), and −1·90br (s; =CH·N=) p.p.m. (rel. int. 3 : 2 : 1). The solid residue was shown by t.l.c. to contain two components; these were separated by column chromatography (type H alumina; elution with methylene chloride) into 4-phenyl-1-(2,3,5,6-tetrafluoro-4-pyridyl)-1,2,3-triazole (0·31 g, 1·10 mmol, total yield 42%) and *5-phenyl-1-(2,3,5,6-tetrafluoro-4-pyridyl)-1,2,3-triazole* (1·1 g, 3·7 mmol, 24%) (Found: C 53·2; H, 2·3; F, 25·4; N, 18·8%), m.p. 127—128 °C (with sublimation), δ_F (ext. $CF_3{\cdot}CO_2H$; saturated soln. in Me_2CO) +11·4 (2-, 6-F) and +69·7 (3-, 5-F) p.p.m. (rel. int. 1 : 1), δ_H (ext. benzene) −0·41 (s, Ph) and −1·09 (s, =CH·N=) p.p.m. (rel. int. 5 : 1).

(f) *With cyclopentadiene dimer.* A solution of 4-azidotetrafluoropyridine (2·0 g, 10·4 mmol) and cyclopentadiene dimer (1·37 g, 10·4 mmol) in light petroleum (b.p. 60—80 °C; 30 ml) was stirred at room temperature for 4 days; a gas, presumed to be nitrogen, was evolved steadily during this period. The solution was then heated under reflux for 1 day. The solvent was removed by distillation, leaving a yellow oil which was subjected to column chromatography (45 × 2·5 cm type H alumina). Elution with light petroleum (b.p. 60—80 °C) provided *9-(2,3,5,6-tetrafluoro-4-pyridyl)-9-azatetracyclo[5,3,1,$0^{2,6}$,$0^{8,10}$]undec-3-ene* (0·96 g, 3·2 mmol, 31%) [Found: C, 60·7; H, 4·2; F, 25·7; N, 9·2%; *M* (mass spec.), 296. $C_{15}H_{12}F_4N_4$ requires C, 60·8; H, 4·1; F, 25·7; N, 9·4%; *M*, 296], m.p. 107—108 °C, δ_F (ext. $CF_3{\cdot}CO_2H$; saturated soln. in CCl_4) +14·3 (2-, 6-F) and +77·7 (3-, 5-F) p.p.m. (rel. int. 1 : 1), δ_H (ext. benzene) 0·93br (s; ·CH:CH·), +3·1 to +4·7 (complex), and +5·2 (AB pattern, *J* 10·3 Hz; CH_2 bridge) p.p.m. (rel. int. 1 : 4 : 1), and a mixture (identified by i.r. and n.m.r. analysis) (0·61 g, 2·1 mmol, 20%) of this azatetracycloundec-3-ene and 8- and/or 9-(2,3,5,6-tetrafluoro-4-pyridylimino)tricyclo[5,2,1,-$0^{2,6}$]dec-3-ene, a sample of which (0·79 g, 2·7 mmol, 26%) (Found: C, 61·2; H, 4·3; F, 23·6; N, 9·3. $C_{15}H_{12}F_4N_2$ requires C, 60·8; H, 4·1; F, 25·7; N, 9·4%), m.p. 77—80 °C (decomp.), $\lambda_{max.}$ 5·92 (C:N str.) μm, δ_F (ext. $CF_3{\cdot}CO_2H$; saturated soln. in CCl_4) +14·0 (2-, 6-F) and +75·7 (3-, 5-F) p.p.m. (rel. int. 1 : 1), δ_H (ext. benzene) +0·9br (s; ·CH:CH·) and +2·8 to +5·3br (complex) p.p.m. (rel. int. 1 : 5), was obtained by further elution of the column with chloroform, which also gave a mixture of 4-amino-2,3,5,6-tetrafluoropyridine and material believed to be tricyclo[5,2,1,$0^{2,6}$]dec-3- and/or 4-en-8-one [0·58 g; $\lambda_{max.}$ 5·76 (C:O str.) μm]. A sample of the 9-(tetrafluoro-4-pyridylimino)tricyclo[5,2,1,-$0^{2,6}$]dec-3-ene isolated was dissolved in ethanol and the solution was warmed with an excess of 4M-hydrochloric acid. The clear solution obtained was stored at room temperature overnight, then neutralised ($NaHCO_3$) and extracted with ether. The extract was dried ($MgSO_4$) and evaporated to give a red oil possessing i.r. spectral properties almost identical with those of the last fraction obtained in the chromatographic separation described.

(g) *With norbornene.* 4-Azidotetrafluoropyridine (2·0 g, 10·4 mmol) was added slowly to a solution of norbornene (1·0 g, 10·6 mmol) in light petroleum (b.p. 40—60 °C; 30 ml); the solution was stored at room temperature for 72 h, during which time 10 mmol of nitrogen was evolved. The solvent was removed by distillation, leaving a yellow oil which was subjected to column chromatography (48 × 2·5 cm type H alumina). Elution with light petroleum (b.p. 60—80 °C) gave *3-(2,3,5,6-tetrafluoro-4-pyridyl)-3-azatricyclo[3,2,1,$0^{2,4}$]-octane* (2·1 g, 8·1 mmol, 76%) (Found: C, 55·5; H, 4·0; N, 10·9. $C_{12}H_{10}F_4N_2$ requires C, 55·8; H, 3·9; N, 10·9%), m.p. 36—38 °C, δ_F (ext. $CF_3{\cdot}CO_2H$; 60% w/w soln. in CCl_4) +13·7 (2-, 6-F) and +76·7 (3-, 5-F) p.p.m. (rel. int. 1 : 1), δ_H (ext. benzene) +3·58br (s; ·CH·N·CH·), +3·82 (s showing signs of splitting, bridgehead >CH), and +4·4 to +8·4 (complex) p.p.m. Further elution with chloroform gave a yellow oil (0·46 g) which was shown by i.r. and n.m.r. spectroscopy (by reference to authentic samples of both compounds) to be a *ca.* 50 : 50 mixture of 4-amino-2,3,5,6-tetrafluoropyridine and bicyclo[2,2,1]heptan-2-one.

(h) *With benzene.* 4-Azidotetrafluoropyridine (5·0 g, 26 mmol) was heated with benzene (156 g, 2·00 mol) in a stainless steel rocking autoclave (250 ml) at 175 °C for 10 h. The black liquid product was evaporated to dryness, leaving a black solid which was sublimed *in vacuo* to provide *4-anilino-2,3,5,6-tetrafluoropyridine* (0·84 g, 3·47 mmol; 13%) (Found: C, 54·2; H, 2·8; N, 11·3. $C_{11}H_6F_4N_2$ requires C, 54·5; H, 2·5; N, 11·6%), m.p. 91 °C, which possessed the same i.r. and n.m.r. spectral characteristics as a sample prepared from pentafluoropyridine and aniline (see later). The black sublimation residue (4·0 g) did not melt below 360 °C and its i.r. spectrum was similar to that of the brown solid obtained by heating 4-azidotetrafluoropyridine alone at 160 °C.

(j) *With cyclohexane.* 4-Azidotetrafluoropyridine (1·0 g, 5·2 mmol) was heated with cyclohexane (42 g, 0·5 mol) at 170 °C for 5 h in a stainless steel rocking autoclave (250 ml). The product, a brown solid suspended in an orange liquid, was filtered. The brown solid did not melt below 360 °C and its i.r. spectrum was similar to that of the amorphous brown solid obtained by heating 4-azidotetrafluoropyridine itself above 160 °C. Distillation of the filtrate provided cyclohexane and a brownish oil which was shown by i.r. spectroscopy and quantitative g.l.c. [2 m silicone SE 30, 185 °C; internal standard 2,3,5,6-tetrafluoro-4-(piperidin-1-yl)pyridine] to comprise 4-amino-2,3,5,6-tetrafluoropyridine (0·03 g, 0·18 mmol, 3%) and 4-cyclohexylamino-2,3,5,6-tetrafluoropyridine (0·58 g, 2·35 mmol, 45%), authentic samples of which were used for calibration purposes.

(k) *With a mixture of cyclo-hexane, -heptane, and -octane.*

A homogeneous mixture of 4-azidotetrafluoropyridine (1·0 g, 5·2 mmol), cyclohexane (21·0 g, 0·25 mmol), cycloheptane (24·5 g, 0·25 mol), and cyclo-octane (28·0 g, 0·25 mol) was heated at 175 °C for 15 h in a stainless steel rocking autoclave (250 ml). The product was filtered to remove a brown-black amorphous solid, m.p. >360 °C, then distilled to yield a brown oil which was shown by a combination of i.r. spectroscopy and quantitative g.l.c. analysis [2 m silicone SE 30, 187 °C; internal standard 2,3,5,6-tetrafluoro-4-(piperidin-1-yl)pyridine] to contain a trace of 4-amino-2,3,5,6-tetrafluoropyridine and 4-cyclohexylamino-, 4-cycloheptylamino-, and 4-cyclo-octylamino-2,3,5,6-tetrafluoropyridine in yields of 0·66 (13%), 1·36 (26%), and 2·10 mmol (40%), respectively. In a duplicate experiment carried out at 175 °C for 22 h, the last three products were formed in yields of 0·53 (10%), 1·07 (21%), and 1·50 mmol (29%), together with a trace of 4-aminotetrafluoropyridine and a black solid (0·19 g).

(l) *With* trans-1,2-*dimethylcyclohexane*. 4-Azidotetrafluoropyridine (2·06 g, 10·7 mmol) in *trans*-1,2-dimethylcyclohexane (50·0 g, 0·45 mol) was heated at 170 °C for 10 h in a stainless steel rocking autoclave (250 ml). The product was worked up as in (k) to give a brown-black solid (0·4 g), m.p. >360 °C, and a brown oil (1·84 g) which was shown by g.l.c. analysis to comprise several components, the major ones being 4-amino-2,3,5,6-tetrafluoropyridine (0·08 mmol, 7%) and the isomeric 1,2-dimethyl-1-(2,3,5,6-tetrafluoro-4-pyridylamino)cyclohexanes (58*A* : 27*B* mixture, 5·7 mmol; 53%) (an authentic mixture was prepared as described later).

(m) *With* cis-1,2-*dimethylcyclohexane*. Experiment (l) was repeated with 1·0 g (5·2 mmol) of 4-azidotetrafluoropyridine and 11·2 g (0·1 mol) of *cis*-1,2-dimethylcyclohexane at 175 °C for 18 h. Work up gave a brown-black solid (0·18 g), m.p. >360 °C, and a brown oil (1·34 g) which was shown by g.l.c. analysis (2 m PEGA, 181 °C) to contain at least five components, the first three to be eluted being 4-amino-2,3,5,6-tetrafluoropyridine (2·8 mmol, 54%) and the isomeric 1,2-dimethyl-1-(2,3,5,6-tetrafluoro-4-pyridylamino)cyclohexanes (15*A* : 32*B* mixture, 2·2 mmol, 42%).

(n) *With* trans-4-*methylpent*-2-*ene*. (i) *At* 175 °C. 4-Azidotetrafluoropyridine (1·08 g, 5·63 mmol) and *trans*-4-methylpent-2-ene (8·4 g, 0·1 mol), which gave only one g.l.c. peak (2 m 5% $AgNO_3$ in $CH_2OH{\cdot}CH_2OH$ on Celite, 21 °C), were heated at 175 °C for 6 h in a stainless steel rocking autoclave (50 ml). The yellow liquid product was distilled to remove unchanged *trans*-4-methylpent-2-ene, and the oily yellow pot residue (1·37 g) (Found: C, 53·3; H, 5·0; F, 30·4; N, 11·1. Calc. for $C_{11}H_{12}F_4N_2$: C, 53·2; H, 4·8; F, 30·7; N, 11·3%) was shown by g.l.c. (2 m Apiezon–Celite, 170 °C) to comprise (in order of increasing retention time) 2-methyl-3-(2,3,5,6-tetrafluoro-4-pyridylimino)pentane (1·88 mmol, 34%), 4-methyl-2-(2,3,5,6-tetrafluoro-4-pyridylimino)pentane (2·82 mmol, 50%), *trans*-2-isopropyl-3-methyl-1-(2,3,5,6-tetrafluoro-4-pyridyl)aziridine (0·77 mmol, 14%), and *cis*-2-isopropyl-3-methyl-1-(2,3,5,6-tetrafluoro-4-pyridyl)-aziridine (0·04 mmol, 0·7%). The product mixture was separated into its components by preparative g.l.c. (6 m PEGA, 180 °C) and the aziridines were identified by comparison of g.l.c. retention times and i.r. and/or n.m.r. spectra with those of authentic samples (see later); the 2-methyl-3-(2,3,5,6-tetrafluoro-4-pyridylimino)pentane [δ_F (ext. $CF_3{\cdot}CO_2H$; soln. in CCl_4) +13·0 (2-, 6-F) and +77·4 (3-, 5-F) p.p.m. (rel. int. 1 : 1), δ_H (100 MHz spectrum, Me_4Si lock) −2·69 (sept, rel. int. 1, Me_2CH), −2·33 (q, rel. int. 2, $MeCH_2$), −1·18 (d, *J* 6·7 Hz, Me_2CH), and −1·13 (t, *J* 7·5 Hz, $MeCH_2$) (total rel. int. of last two absorptions 9) p.p.m.] and 4-methyl-2-(2,3,5,6-tetrafluoro-4-pyridylimino)pentane were identified by n.m.r. spectroscopy, the latter being examined as a *ca.* 2 : 1 mixture [$\lambda_{max.}$ (film) 5·98 (C:N str.) μm] with the former owing to separation difficulties. The ^{19}F spectrum of the *ca.* 2 : 1 mixture as a solution in carbon tetrachloride showed absorptions at 13·0 (2-, 6-F of both isomers), 76·7 (3-, 5-F of the 4-methyl compound), and 77·4 (3-, 5-F of the 2-methyl isomer) p.p.m. to high field of external $CF_3{\cdot}CO_2H$; the ^1H spectrum (100 MHz, Me_4Si lock) showed a 6·5 Hz doublet at −0·96 p.p.m. ($Me_2CH{\cdot}CH_2$) which almost obscured the highest field component of the −1·13 triplet of the 2-methyl isomer, and a broadened singlet at −1·95 p.p.m. (MeC:N) on the high-field edge of a complex absorption stretching downfield to the clearly observable −2·69 p.p.m. septet caused by the 2-methyl isomer.

(ii) *At* 65 °C. A mixture of 4-azidotetrafluoropyridine (3·0 g, 15·6 mmol) and *trans*-4-methylpent-2-ene (8·4 g, 0·1 mol) was heated under reflux (bath temp. 65 °C) for 8 h (until evolution of nitrogen ceased). The product was examined as in the experiment at 175 °C and found to comprise 2-methyl-3-(2,3,5,6-tetrafluoro-4-pyridylimino)pentane (5·8 mmol, 37%), 4-methyl-2-(2,3,5,6-tetrafluoro-4-pyridylimino)pentane (8·2 mmol, 52%), and *trans*-2-isopropyl-3-methyl-1-(2,3,5,6-tetrafluoro-4-pyridyl)aziridine (1·4 mmol, 9%).

Preparation of Amines from Pentafluoropyridine.—(a) 4-*Anilino*-2,3,5,6-*tetrafluoropyridine*. A solution of freshly distilled aniline (1·10 g, 11·8 mmol) in acetone (10 ml) was added dropwise to a vigorously stirred solution of pentafluoropyridine (2·00 g, 11·8 mmol) in acetone (15 ml) containing sodium carbonate (2·2 g). The mixture was heated under reflux for 4 h, cooled, filtered, and evaporated to give a yellow oil which slowly solidified. Recrystallisation from light petroleum (b.p. 60—80 °C) provided 4-anilino-2,3,5,6-tetrafluoropyridine (0·3 g, 1·2 mmol, 10%) [Found: C, 54·2; H, 2·6; N, 11·8%; *M* (mass spec.), 242. Calc. for $C_{11}H_6F_4N_2$: C, 54·2; H, 2·5; N, 11·6%; *M*, 242], m.p. 90—92 °C, $\lambda_{max.}$ (mull) 3·03 (N–H str.) μm, δ_F (ext. $CF_3{\cdot}CO_2H$; 30% w/w soln. in hexamethylphosphoramide) +17·2 (2-, 6-F) and +76·0 (3-, 5-F) p.p.m. (rel. int. 1 : 1), δ_H (ext. benzene) −0·57br (s, Ph) and −3·88br (s, NH) p.p.m. (rel. int. 5 : 1).

A higher yield of the anilino-derivative was obtained by treating a solution of pentafluoropyridine (3·00 g, 17·7 mmol) in tetrahydrofuran (30 ml) with a slurry of the sodium salt of aniline [from aniline (1·66 g, 17·8 mmol) and sodamide (0·70 g, 18·0 mmol)] in tetrahydrofuran (60 ml) under nitrogen. The mixture was stirred at room temperature for 2 h then poured into water (1500 ml). The aqueous solution was extracted with ether (3 × 150 ml), and the extract was dried ($MgSO_4$) and evaporated under reduced pressure; vacuum sublimation of the residue yielded 4-anilino-2,3,5,6-tetrafluoropyridine (1·01 g, 4·20 mmol, 24%), m.p. and mixed m.p. 90—92 °C, identified by i.r. and ^{19}F n.m.r. spectroscopy.

(b) 4-*Cyclohexylamino*-2,3,5,6-*tetrafluoropyridine*. Cyclohexylamine (5·88 g, 59·4 mmol) was added slowly to a vigorously stirred solution of pentafluoropyridine (5·00 g, 29·6 mmol) in acetonitrile (40 ml). The mixture was stirred for 1 h then poured into water (300 ml). 4-*Cyclohexylamino*-2,3,5,6-*tetrafluoropyridine* (5·05 g, 20·4 mmol 69%) [Found: C, 53·4; H, 4·8; N, 11·5%; *M* (mass spec.), 248. $C_{11}H_{12}F_4N_2$ requires C, 53·2; H, 4·8; N, 11·3%; *M*, 248], m.p. 50—52 °C, b.p. 120—121 °C at 4 mmHg, $\lambda_{max.}$ (melt) 2·93m—w, 3·00w,br (free and H-bonded N–H str., respectively) μm, δ_F (ext. $CF_3{\cdot}CO_2H$; 42% w/w soln. in CCl_4) +18·3 (2-, 6-F) and

+88·0 (3-, 5-F) p.p.m. (rel. int. 1 : 1), δ_H (ext. benzene) +2·02br (s, NH), +2·8br (s, C*H*·NH), and +4·2 to +5·6 (complex, ring CH_2) p.p.m. (rel. int. 1 : 1 : 10), was isolated by ether extraction and subsequent distillation.

(c) 4-*Cycloheptylamino*-2,3,5,6-*tetrafluoropyridine*. By use of the method described in (b), pentafluoropyridine (5·00 g, 29·6 mmol) was treated with cycloheptylamine (6·70 g, 59·3 mmol) in acetonitrile (50 ml) to provide 4-*cycloheptylamino*-2,3,5,6-*tetrafluoropyridine* (3·80 g, 14·5 mmol, 49%) [Found: C, 54·9; H, 5·4; N, 10·8%; *M* (mass spec.), 262. $C_{12}H_{14}F_4N_2$ requires C, 54·9; H, 5·3; N, 10·7%; *M*, 262], b.p. 92—94 °C at 0·2 mmHg, $\lambda_{max.}$ (film) 2·92m—w, 2·99w,br (free and H-bonded N–H str., respectively; a very dilute solution of the amine in carbon tetrachloride solution showed only a band at 2·92), 6·07vs, 6·49s, and 6·74vs (polyfluorinated pyridine nucleus) μm, δ_F (ext. $CF_3{\cdot}CO_2H$; neat liquid) +16·5 (2-, 6-F) and +86·9 (3-, 5-F) p.p.m. (rel. int. 1 : 1), δ_H (ext. benzene) +1·7 to +2·1br (d, NH), +2·5 to 3·1br (s, C*H*·NH), and +4·3 to +5·4 (complex, ring CH_2) p.p.m. (rel. int. 1 : 1 : 12).

(d) 4-*Cyclo-octylamino*-2,3,5,6-*tetrafluoropyridine*. By use of the method described in (b), pentafluoropyridine (5·00 g, 29·6 mmol) was treated with cyclo-octylamine (7·50 g, 59·2 mmol) in acetonitrile (50 ml) to give 4-*cyclo-octylamino*-2,3,5,6-*tetrafluoropyridine* (5·80 g, 21·0 mmol, 71%) [Found: C, 56·5; H, 5·8; N, 10·1%; *M* (mass spec.), 276. $C_{13}H_{16}F_4N_2$ requires C, 56·5; H, 5·8; N, 10·2%; *M*, 276], b.p. 118—120 °C at 0·4 mmHg, $\lambda_{max.}$ (film) 2·92m—w, 2·99w,br (free and H-bonded N–H str., respectively; a very dilute solution of the amine in carbon tetrachloride showed only a band at 2·92) μm, δ_F (ext. $CF_3{\cdot}CO_2H$; 60% w/w soln. in CCl_4) +17·3 (2-, 6-F) and +86·7 (3-, 5-F) p.p.m. (rel. int. 1 : 1), δ_H (ext. benzene) +1·85br (d, NH), +2·55br (s, C*H*·NH), and +4·93 (basically br,s, ring CH_2) p.p.m. (rel. int. 1 : 1 : 14).

(e) cis- *and* trans-1,2-*Dimethyl*-1-(2,3,5,6-*tetrafluoro*-4-*pyridylamino*)*cyclohexane*. A 1 : 1 mixture of *cis*- and *trans*-1-amino-1,2-dimethylcyclohexane [21] (2·0 g, 15·7 mmol) was added dropwise to a cold (0 °C) stirred mixture of pentafluoropyridine (2·64 g, 15·6 mmol) and sodium carbonate (1·7 g) in acetonitrile (20 ml). The cold mixture was stirred for 1 h, warmed to 21 °C, and stirred for 3 h, then poured into water (1 l). The aqueous solution was extracted with ether (3 × 100 ml), and the extract was dried ($MgSO_4$) then evaporated under reduced pressure; the yellow oily residue was distilled to give a 57 : 43 (ratio of g.l.c. peaks; 3 m silicone SE 30, 197 °C) mixture of isomeric 1,2-dimethyl-1-(2,3,5,6-tetrafluoro-4-pyridylamino)cyclohexanes (1·7 g, 6·2 mmol, 40%) [Found: C, 56·5; H, 5·8; N, 10·4%; *M* (mass spec.), 276. Calc. for $C_{13}H_{16}F_4N_2$: C, 56·5; H, 5·8; N, 10·2%; *M*, 276], b.p. 120 °C at 1·5 mmHg, $\lambda_{max.}$ (film) 2·92m, 2·99w,br,sh (free and H-bonded N–H str., respectively) μm.

(f) cis-2-*Isopropyl*-3-*methyl*-1-(2,3,5,6-*tetrafluoro*-4-*pyridyl*)*aziridine*. An ethereal solution (50 ml) of 2-azido-3-iodo-4-methylpentane, obtained by ether extraction of the product formed by attack of iodine azide on *cis*-4-methylpent-2-ene (4·2 g, 0·05 mol),[22a] was treated with lithium aluminium hydride to yield *cis*-2-isopropyl-3-methylaziridine; [22b] this was not isolated but converted into its *N*-lithio-derivative by reaction with n-butyl-lithium. The ethereal solution thus obtained was added gradually to a cold (−20 °C) stirred solution of pentafluoropyridine (8·45 g, 0·05 mol) in ether (30 ml), and the resulting orange liquid was warmed to 21 °C, stirred for 1 h, then shaken with water (200 ml). The ether layer was dried ($MgSO_4$) and then distilled, to give cis-2-*isopropyl*-3-*methyl*-1-(2,3,5,6-*tetrafluoro*-4-*pyridyl*)*aziridine* (0·99 g) (Found: C, 52·7; H, 5·0; N, 11·3 $C_{11}H_{12}F_4N_2$ requires C, 53·2; H, 4·8; N, 11·3%), b.p. 74—78 °C at 1·5 mmHg, which crystallised (m.p. 35—36 °C) on storage at room temperature.

A superior method comprised preparation of *cis*-2-isopropyl-3-methylaziridine (18% yield), b.p. 40—42 °C at 31 mmHg (lit.,[23] 38—39 °C at 30 mmHg), *via* reaction of *cis*-4-methylpent-2-ene with iodine cyanate,[23] followed by dropwise addition of a solution of this aziridine (2·0 g, 20 mmol) in acetonitrile (15 ml) to a cold (−20 °C) solution of pentafluoropyridine (3·4 g, 20 mmol) in acetonitrile (30 ml) containing sodium carbonate (2·4 g). The mixture was stirred at −20 °C for 1 h then at 21 °C for 15 h before being poured into water (800 ml). Ether extraction (3 × 150 ml) followed by distillation gave *cis*-2-isopropyl-3-methyl-1-(2,3,5,6-tetrafluoro-4-pyridyl)aziridine * (3·12 g, 12·6 mmol, 62%) [Found: C, 53·0; H, 4·7; N, 11·0%; *M* (mass spec), 248. Calc. for $C_{11}H_{12}F_4N_2$: C, 53·2; H, 4·8; N, 11·3%; *M*, 248], m.p. 35—37 °C, b.p. 88—90 °C at 2·5 mmHg, δ_F (ext. $CF_3{\cdot}CO_2H$; neat liq.) +16·0 (2-, 6-F) and +78·0 (3-, 5-F) p.p.m. (rel. int. 1 : 1), δ_H (ext. benzene; soln. in CCl_4) +4·2 (complex, Me$\overline{C\mathit{H}{\cdot}N{\cdot}CH}$Pr^i), +4·4 (complex, Me$\overline{CH{\cdot}N{\cdot}C\mathit{H}}$Pr^i), *ca.* 5·0 (complex, partly obscured by the next higher field band, C*H*Me$_2$), +5·19 (d, *J* 5·5 Hz, *Me*$\overline{CH{\cdot}N{\cdot}CH}$Pr^i), +5·35 (d, *J* 6·3 Hz, with further splitting), and +5·57 (d, *J* 6·6 Hz) (the last two are assigned to the non-equivalent Me groups of the Pr^i) p.p.m. Spin-decoupling experiments on the +4·2 and +4·4 p.p.m. multiplets (complex AB sub-spectra, J_{AB} 6·4 Hz) confirmed these assignments.

(g) trans-2-*Isopropyl*-3-*methyl*-1-(2,3,5,6-*tetrafluoro*-4-*pyridyl*)*aziridine*. *trans*-2-Isopropyl-3-methylaziridine, b.p. 34—35 °C at 31 mmHg (lit.,[23] 36 °C at 30 mmHg), prepared from iodine cyanate and *trans*-4-methylpent-2-ene,[23] was used (2·0 g, 20 mmol) to convert pentafluoropyridine (3·4 g, 20 mmol) into the corresponding aziridine, as in the second experiment in (f). The oil obtained by distillation of the product was shown by g.l.c. to contain several components; the major one was separated by preparative g.l.c. (3·5 m Apiezon–Celite, 160 °C) and shown to be trans-2-*isopropyl*-3-*methyl*-1-(2,3,5,6-*tetrafluoro*-4-*pyridyl*)*aziridine* * (2·4 g, 9·5 mmol, 47%) (Found: C, 53·2; H, 4·5; F, 30·6; N, 11·1. Calc. for $C_{11}H_{12}F_4N_2$: C, 53·2; H, 4·8; F, 30·7; N, 11·3%), δ_F (ext. $CF_3{\cdot}CO_2H$; 60% soln. w/w in CCl_4) +16·0 (2-, 6-F) and +78·8 (3-, 5-F) p.p.m. (rel. int. 1 : 1), δ_H (ext. benzene) +3·9 (complex, Me$\overline{C\mathit{H}{\cdot}N{\cdot}CH}$Pr^i), +4·5 (complex, Me$\overline{CH{\cdot}N{\cdot}C\mathit{H}}$Pr^i), +4·97br (sept, C*H*Me$_2$), +5·34 (d, *J* 5·5 Hz, with further splitting, *Me*$\overline{CH{\cdot}N{\cdot}CH}$Pr^i), +5·52 (d, *J* 6·6 Hz), and +5·61 (d, *J* 6·8 Hz) (the last two are assigned to the non-equivalent Me groups of Pr^i) p.p.m. (rel. int. 1 : 1 : 1 : 3 : 6). Spin-decoupling experiments on the two low-field multiplets confirmed the assignments.

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[21] Prepared as described by K. E. Hamlin and M. Freifelder, *J. Amer. Chem. Soc.*, 1953, **75**, 369.

[22] The method employed is described (*a*) by F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, 1967, **89**, 2077, and (*b*) by A. Hassner, G. J. Matthews, and F. W. Fowler, *ibid.*, 1969, **91**, 5046.

[23] G. Swift and D. Swern, *J. Org. Chem.*, 1967, **32**, 511.