Fluorinations with Potassium Tetrafluorocobaltate(III). Part VI.[1] Fluorination of Pyridine and 4-Methylpyridine

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Pyridine has been fluorinated over $KCo^{III}F_4$ to give a mixture largely of ring-opened products. The main components isolated were (*Z*)-undecafluoro-2-azahex-2-ene (I), (*Z*)-2*H*-1-bistrifluoromethylaminotetrafluoroprop-1-ene (II), (*E*)-2*H*-1-bistrifluoromethylaminotetrafluoroprop-1-ene (III), (*Z*)-5*H*-decafluoro-2-azahex-2-ene (IV), (2*Z*,4*E*)-4*H*,5*H*-heptafluoro-2-azahexa-2,4-diene (V), (2*Z*,4*Z*)-5*H*-octafluoro-2-azahexa-2,4-diene (VI), (2*Z*,4*E*)-5-bistrifluoromethylamino-octafluoro-2-azahexa-2,4-diene (VII), (2*Z*,4*Z*)-5-bistrifluoromethylamino-octafluoro-2-azahexa-2,4-diene (VIII), and 3*H*-1-difluoromethylheptafluoropyrrolidine(IX). In a similar manner, fluorination of 4-methylpyridine gave the analogous compounds (*Z*)-5-trifluoromethyldecafluoro-2-azahex-2-ene (X), (*Z*)-5-trifluoromethyloctafluoro-2-azahexa-2,4-diene (XI), (*Z*)-5-methyldecafluoro-2-azahex-2-ene (XII), and (*Z*)-5-difluoromethyldecafluoro-2-azahex-2-ene (XIII) as major components.

IN previous papers in this series we have described the fluorinations of benzene,[2] naphthalene,[3] ketones,[4] and esters and acid fluorides [5] by $KCo^{III}F_4$, the results differing significantly from those obtained using CoF_3. We have now extended our studies of the former reagent to the fluorination of pyridine and 4-methylpyridine.

Although pyridine and its derivatives have successfully been fluorinated by the electrochemical method [6] to give polyfluoropiperidines, and various polyfluoropyridines were prepared by exchange processes,[7] attempts to fluorinate pyridines by using transition metal fluorides have given poor results. Pyridine and CoF_3 at 350° gave [8] perfluoropiperidine as the only isolable product in 0·2% yield, 2,6-dimethylpyridine giving [9] a 5% yield of the corresponding perfluoropiperidine. In related work [10] 2-fluoropyridine with elemental fluorine yielded a complex mixture of breakdown products and a little perfluoropiperdine.

We have found that fluorination of pyridine over the new reagent $KCoF_4$ at 210—230° gave a complex mixture of products containing nine main components. Separation of the mixture was difficult since some decomposition with deposition of crystals occurred on standing even for a short time at room temperature, and also normal fractional distillation gave rise to extensive decomposition. The mixture was finally fractionated into cuts each of which contained a substantial percentage of one of the major components, by using rapid take-off and careful heating on an oil-bath, so as to keep the flask temperature to a minimum. Further purification could be carried out by g.l.c. and the nine major components were all isolated (see the Table). The crystals formed on decomposition were identified by elemental analysis and spectroscopy as 4,4,4-trifluoro-*N*-trifluoromethylcrotonamide which presumably arises from hydrolysis of compound (V) (see below).

The lowest boiling component was shown by comparison of its i.r. and n.m.r. spectra to be the known undecafluoro-2-azahex-2-ene (I) with a chemical shift value for the imino-trifluoromethyl groups in agreement with that given by Haszeldine [11] rather than that of Muller.[12] On the basis of the ^{19}F n.m.r. spectrum we assign the stereochemistry of the $CF_3N{=}CF$ double bond as *Z*.[13] The reasoning follows that of Ogden and Mitsch [14] for compounds containing the $CF_3N{=}CF$ group. By analogy with fluoro-olefins, where the CF_3 groups showed a signal in the range 57·3—57·7 p.p.m. (shift relative to CCl_3F) with a doublet splitting of 13·3—14·3 Hz they ascribed *cis* (*Z*) stereochemistry, whilst where peaks occurred at 54·2—56·8 p.p.m. with a coupling of *ca.* 6 Hz, *trans* (*E*) stereochemistry was assumed. In compound (I), resonance occurred at 57·3 p.p.m. with a coupling of 14 Hz, indicating that the compound had *Z* stereochemistry. This pattern was repeated for all the imines isolated from this fluorination.

The i.r. spectrum of the second component isolated (II) indicated that there was no $CF_3N{=}CF$ group since the band at *ca.* 1770 cm^{-1} [14] was absent, but a band at 1725 cm^{-1} suggested a $CH{=}CF$ group. Oxidation of (II) with potassium permanganate in acetone afforded trifluoroacetic acid, identified as its *S*-benzylisothiouronium salt, suggesting the presence of a vinylic CF_3 group. The mass spectrum gave a peak at *m/e* 246 and a fragmentation pattern consistent with the structure $(CF_3)_2NCF{=}CHCF_3$ (II). This was supported by elemental analysis, and ^1H and ^{19}F n.m.r. spectral analysis. The stereochemistry of the double bond was indicated by the n.m.r. spectra. The olefinic proton showed two couplings, 21·8 and 6·5 Hz, the value 21·8

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[1] Part V, J. Burdon, J. R. Knights, I. W. Parsons, and J. C. Tatlow, *J. Fluorine Chem.*, in the press.

[2] P. L. Coe, R. G. Plevey, and J. C. Tatlow, *J. Chem. Soc.* (*C*), 1969, 1060.

[3] P. L. Coe, R. M. Habib, and J. C. Tatlow, in preparation.

[4] R. D. Bagnall, P. L. Coe, and J. C. Tatlow, *J.C.S. Perkin I*, 1972, 2277.

[5] R. D. Bagnall, P. L. Coe, and J. C. Tatlow, submitted for publication in *J. Fluorine Chem.*

[6] J. H. Simons, *J. Electrochem. Soc.*, 1949, **95**, 47.

[7] R. D. Chambers, J. Hutchinson, and W. K. R. Musgrave, *J. Chem. Soc.*, 1964, 3573.

[8] R. N. Haszeldine, *J. Chem. Soc.*, 1950, 1966.

[9] R. N. Haszeldine, *J. Chem. Soc.*, 1950, 1638.

[10] R. E. Banks and G. E. Williamson, *J. Chem. Soc.*, 1965, 815.

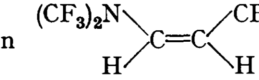
[11] R. E. Banks, W. M. Cheng, and R. N. Haszeldine, *J. Chem. Soc.*, 1962, 3407.

[12] N. Muller, P. C. Lauterbauer, and C. F. Svatos, *J. Amer. Chem. Soc.*, 1957, **79**, 1807.

[13] J. E. Blackwood, C. L. Gladys, K. L. Loering, A. E. Petranca, and J. E. Rush, *J. Amer. Chem. Soc.*, 1968, **90**, 509.

[14] P. H. Ogden and R. A. Mitsch, *J. Amer. Chem. Soc.*, 1967, **89**, 5007.

lying in the range expected for a *trans* HF system.[15] The ^{19}F spectrum showed couplings for the CF_3 group of 17·8 (coupling with the vinylic fluorine atom) and 6·6 Hz (see above in the ^{1}H spectrum) due to geminal CF_3–H coupling. This latter corresponds well to the value found[16] in

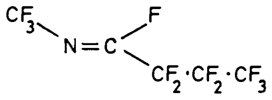
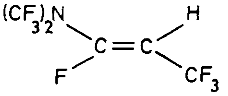
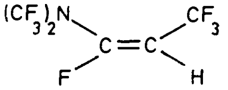
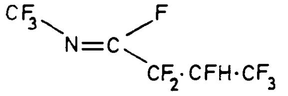
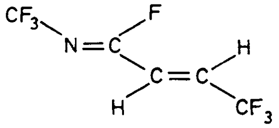
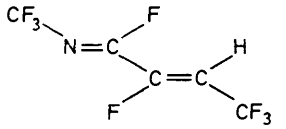
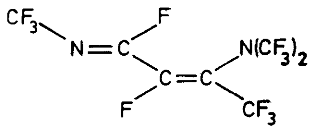
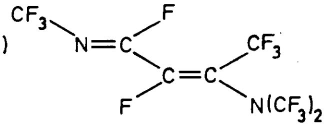
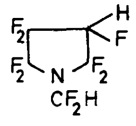
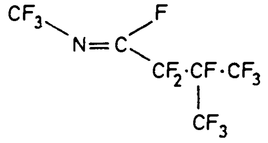
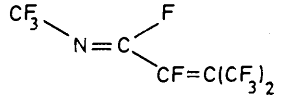
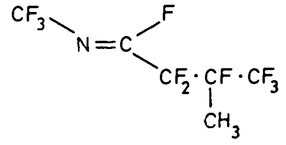
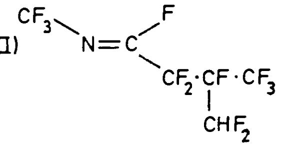


$(CF_3)_2N(H)C{=}C(H)CF_3$

of 6·3 Hz. We thus assign *Z* stereochemistry to compound (II).

The third component isolated (III) showed very similar mass spectral, i.r., and analytical data to compound (II) above, but showed differences in the ^{1}H and ^{19}F n.m.r. spectra. Oxidation as above again afforded trifluoroacetic acid. The olefinic proton showed couplings of 6 and 3·25 Hz whilst in the ^{19}F spectrum the CF_3 group and olefinic fluorine atom gave complex peaks. However, on the basis of the ^{1}H spectrum it is clear that a geminal CF_3–H coupling (6 Hz) is present, and the 3·25 Hz coupling is consistent with a *cis*-H–F grouping.[15] Thus compound (III) is assigned *E* stereochemistry.

Composition of fluorination mixture from $KCo^{III}F_4$ and pyridine or 4-methylpyridine

Product		Yield (%) *
	Pyridine	
(I)		15·4
(II)		6·3
(III)		5·6
(IV)		11·5
(V)		8·2
(VI)		19·4
(VII)		1·5
(VIII)		1·4
(IX)		2·1
Residue		28·5
	4-Methylpyridine	
(X)		6·9
(XI)		9·8
(XII)		17·6
(XIII)		10·1
Residue		55·9

* Based on isolated products.

The fourth component (IV) showed an i.r. band at 1770 cm^{-1}, indicating the presence of a $CF_3N{=}CF$ group, confirmed by the ^{19}F n.m.r. spectrum which showed the characteristic peak for the CF_3 group at 58·3 p.p.m. with a 14 Hz coupling as discussed above. The mass spectrum and elemental analysis data suggested a structure $CF_3N{=}CFC_3HF_6$. The ^{19}F n.m.r. spectrum showed a peak at 213·2 p.p.m., corresponding to a –CFH group rather than a –CF_2H group. A 5*H*- rather than a 4*H*-arrangement is preferred on the basis of coupling patterns * so the structure of (IV) is (*Z*)-$CF_3N{=}CFCF_2CHFCF_3$.

The fifth and sixth components (V) and (VI) were difficult to separate, but by careful preparative g.l.c. each was obtained pure. Compound (V) showed two i.r. bands at 1730 and 1670 cm^{-1} assigned to $CF_3N{=}CF$– and –CH=CH– respectively. Elemental analysis and mass spectral data suggested $C_5H_2F_7N$ as the empirical formula indicating (V) to be a hexadiene. The ^{1}H n.m.r. spectrum showed a complex system attributable

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* The ^{1}H and ^{19}F n.m.r. data are listed in a Supplementary Publication: see the Experimental section.

[15] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution N.M.R.,' Pergamon, Oxford, 1966.

[16] J. Freear and A. E. Tipping, *J. Chem. Soc.* (*C*), 1968, 1096

to an $ABMX_3$ system[17] from which J_{AB} could be determined as 16 Hz. This value suggests that the vinylic hydrogen atoms are in the *E* arrangement on the basis that J_{HH} (*trans*) in olefinic compounds usually falls in the range 13—18 Hz. The $CF_3N=CF$ group showed the typical 14 Hz coupling noted in all the previous compounds and is characteristic of the *Z* configuration. Thus (V) is assigned the structure (2*Z*,4*E*)-4*H*,5*H*-heptafluoro-2-azahexa-2,4-diene. Compound (VI) showed bands in its i.r. spectrum which suggested the presence of $CF_3N=CF-$ (1740) and $-CF=CH$ (1690 cm^{-1}) groups. Mass spectral and analytical data indicated that (VI) was C_5HF_8N. The ^1H n.m.r. spectrum indicated that the product contained a single vinylic proton coupled to a geminal CF_3 group (7 Hz) and to a *trans*-fluorine atom (26 Hz), and the ^{19}F n.m.r. spectrum confirmed this and indicated the characteristic coupling for the $CF_3N=CF-$ group; (VI) is thus assigned as (2*Z*,4*Z*)-5*H*-octafluoro-2-azahexa-2,4-diene.

Compounds (VII) and (VIII) were very similar. Mass spectral and analytical data suggested an empirical formula $C_7F_{14}N_2$; the ^1H n.m.r. spectrum confirmed to absence of protons. The ^{19}F n.m.r. spectrum indicated that each compound had the (*Z*)-$CF_3N=CF$ group. The remaining signals suggested the presence of CF_3, $=CF$, and $(CF_3)_2N$ groups. Thus (VII) and (VIII) appeared to be isomers differing in the configuration about a double bond and to have the gross structure $CF_3N=CFCF=CCF_3N(CF_3)_2$. Analysis of the coupling patterns found for the vinylic CF_3 and F groups, showed a doublet for the CF_3 group in (VII) (J_{FF} 17 Hz) but a complex pattern for the CF_3 group in (VIII) whilst the vinylic F atom in (VII) gave a doublet of quartets [$J_{FF}(d) = J_{FF}(q) = 17$ Hz] but a broad singlet in (VIII). On this basis (VII) is assigned the *E* configuration about the C=C bond whilst (VIII) has the *Z* arrangement.

The final component isolated (IX) was shown by analytical and mass spectral data to be $C_5H_2F_9N$ with a breakdown pattern very different from that of compounds (I)—(VIII) suggesting a different type of structure. The ^1H n.m.r. spectrum showed a signal attributable to a CF_2H group (J_{HF} 58 Hz) and another proton doubly split (J_{HF} 51 Hz). The ^{19}F n.m.r. spectrum also showed the CF_2H group but gave a quintet splitting in addition to the large doublet expected for the H–F coupling. Further, the spectrum revealed two AB type signals and a collapsed AB, each corresponding to the fluorine atoms. There was also a high field signal due to a single fluorine atom (CFH group). This suggested that (IX) could be 1-difluoromethyl-3*H*-heptafluoropyrrolidine, and this was subsequently confirmed in an independent preparation by fluorination of *N*-methylpyrrole.[18]

The original fluorination mixture also contained a high boiling fraction now shown[19] to contain several polyfluoropyridines. The compounds isolated from this fluorination are of interest, as is the route by which they are formed. In an attempt to relate positions in the ring-opened products to those in pyridine, we next fluorinated 4-methylpyridine under essentially the same conditions. A complex mixture resulted, since CH_3, CH_2F, CF_2H, and CF_3 groups can be formed from the methyl group. However, four major components, constituting 45—50% of the mixture were isolated. By a combination of analytical and spectral measurements, applying the arguments used above (see Experimental section for details) these were assigned structures (X)—(XIII) (see Table). Thus, the 4-methyl group in the starting material ends up in the 5-position in all the products isolated.

The reaction pathways which give rise to these products are not yet understood. Three different species are formed, polyfluoropyridines,[19] the open-chain compounds described herein, and the ring contracted *N*-methylpyrrolidine derivative. Fluorination of pyridine and methylpyridines with caesium tetrafluorocobaltate(III) affords[20] polyfluoro-pyridines and -*N*-methylpyrrolidines, the latter being major products, but no open-chain compounds have been detected so far.

In the previous fluorination of aromatic compounds we have postulated that in the initial stages of the reaction the transition metal fluoride, *e.g.* CoF_3, acts as an oxidising agent to produce radical cations by attack on the π system,[1,3,21] very much in the manner postulated for the formation of phenols from aqueous cobaltic salt oxidation of arenes. The radical cations are then assumed to be attacked by fluorine atoms or fluoride ions to lead either by loss of a proton or by further oxidation and loss of a proton to aromatic compounds, *e.g.* $C_6H_6 \longrightarrow C_6H_5F \longrightarrow p\text{-}C_6H_4F_2$. It is possible in this way by successive oxidations and reaction of the radical ions to explain the formation of the observed products. Application of this analysis to the fluorination of pyridine suggests that 2,3,5,6-tetrafluoropyridine should be a key intermediate in the fluorination. This isomer is found as a significant product in the higher boiling fractions of pyridine–$KCoF_4$ fluorination[19] and it has subsequently been shown that on fluorination it leads to the expected products.[19]

Further support for this idea comes from electrochemical methoxylation of 2,6-dimethoxypyridine which leads to 2,3,5,6-tetramethoxypyridine and 2,3,3,6,6-pentamethoxyazacyclohexa-1,4-diene.[22] This latter compound corresponds to 1,1,4,4-tetrafluorocyclohexa-1,4-diene found in the fluorination of benzene with $KCoF_4$.[2]

Pyrolyses of perfluorinated heterocycles with N–F bonds, *e.g.* perfluoropiperidine, have been re-

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[17] J. Burdon, personal communication.

[18] P. L. Coe, P. Smith, and J. C. Tatlow, unpublished work.

[19] P. L. Coe, A. G. Holton, and J. C. Tatlow, unpublished work.

[20] A. J. Edwards, R. G. Plevey, I. J. Sallomi, and J. C. Tatlow, *J.C.S. Chem. Comm.*, 1972, 1028.

[21] J. Burdon, I. W. Parsons, and J. C. Tatlow, *Tetrahedron*, 1972, **28**, 43.

[22] N. L. Weinberg and E. A. Brown, *J. Org. Chem.*, 1966, **31**, 4054.

ported,[10,11,23] and open-chain products and perfluoro-*N*-methylpyrrolidine were formed. Alternative free radical mechanisms were proposed for these processes. However, we have so far not detected any cyclic products containing N–F bonds in our fluorination mixtures and since the reaction temperatures we have used are much lower than those used in the pyrolyses, such mechanisms may well not be operating.

The gross structures of products (I), (IV)—(VI), and (X)—(XIII) obtained from pyridine and 4-methylpyridine indicated the rupture of the 2,3 bond in the ring to be important. It seems possible that this occurs following the formation of an $N–C_3$ bond to give rise to the *N*-methylpyrrolidine (IX) obtained. Products (VII) and (VIII) presumably arise by the incorporation of $(CF_3)_2N$ [*via* $(CF_3)_2NH$?] into a C–N–C_4 unit [(VI)?]. Compounds (II) and (III) might arise from re-incorporation in a different way of a $(CF_3)_2N$ unit into the C_3 unit left when it is formed, or could come from breakdown of the orginal heterocyclic ring in a different way.

EXPERIMENTAL

Apparatus.—Fluorinations were carried out in a conventional reactor, as previously described,[2] containing potassium tetrafluorocobaltate(III) (6·5 kg). Preparative g.l.c. utilised two columns: Unit A; dinonyl phthalate–Celite 1 : 2 (488 × 3·5 cm), and Unit B; dinonyl phthalate (920 × 1 cm), on a Pye series 104 instrument. The ^1H and ^{19}F n.m.r. data of compounds (II)—(XIII) are listed in Supplementary Publication No. SUP 21025 (5 pp.).*

Fluorination of Pyridine.—In a typical run, pyridine (100 g) was added to the reactor at 210—230° in a stream of nitrogen (10 l h^{-1}) over 3 h. After the addition, nitrogen was passed for a further 2 h. The effluent gases were passed through a sodium fluoride pellet trap at 85—90° and then collected in a glass trap cooled in liquid air to give products (145 g). After a short time crystals appeared in the fluorination mixture. Sublimation in vacuo afforded 4,4,4-*trifluoro*-N-*trifluoromethylcrotonamide*, m.p. 122—123° (Found: C, 29·0; H, 1·5; F, 55·6; N, 6·8. $C_5H_3F_6NO$ requires C, 29·0; H, 1·4; F, 55·1; N, 6·8%), τ −0·1 (1H, s, CF_3NH) and 3·12 (2H, complex, –CH=CH–), ^{19}F n.m.r. 57·9 (d, J_{HF} 3 Hz, CF_3–NH) and 66·2 p.p.m. (rel. to CCl_3F) (d, J_{HF} 5·5 Hz, CF_3–CH=).

Fractional Distillation.—The products (576 g) from four fluorinations were filtered through layers of sodium fluoride and magnesium sulphate and then carefully distilled through a vacuum jacketed column (122 × 2·5 cm) packed with Dixon gauze rings to give the fractions 1—6 described below; at *ca*. 70° degradation occurred and fractions 7 (97 g) and 8 (49·9 g) were obtained by distillation *in vacuo*; a residue (196 g) remained.

Isolation of Products.—*Fraction* 1 (b.p. <45°, 62·6 g). Separation of the part fraction (15 g) by g.l.c. (Unit A, 75°, N_2 10 l h^{-1}) gave (i) (*Z*)-undecafluoro-2-azahex-2-ene (I) (8·9 g), b.p. 39—40° (lit.,[11] 39°) (Found: C, 21·4; F, 73·4. Calc. for $C_5H_{11}N$: C, 21·2; F, 73·9%), *m*/*e* 283 (M^+), 264 ($C_5F_{10}N^+$), 214 ($C_4F_8N^+$), 164 ($C_3F_6N^+$), and 114 ($C_2F_4N^+$). The i.r. and ^{19}F n.m.r. spectra[11] were in agreement with published data; (ii) a mixture of two components (4·6 g) of which 1 g was further separated (Unit B, 55°, N_2 0·35 kg cm^{-2}) into (a) (Z)-1-*bistrifluoromethylamino*-2H-*tetrafluoroprop*-1-*ene* (II) (0·5 g), b.p. 43° (Found: C, 22·4; H, 0·5; F, 71·6. $C_5HF_{10}N$ requires C, 22·6; H, 0·4; F, 71·7%), $\nu_{max.}$ 1725 cm^{-1} (–CF=CH–), *m*/*e* 246 (*M* − 19), 196 ($C_4HF_5N^+$), 177 ($C_4HF_6N^+$), and 158 ($C_4HF_5N^+$), and (b) (E)-1-*bistrifluoromethylamino*-2H-*tetrafluoroprop*-1-*ene* (III) (0·3 g), b.p. 44° (Found: C, 22·8; H, 0·6; F, 71·2. $C_5HF_{10}N$ requires C, 22·6; H, 0·4; F, 71·7%), $\nu_{max.}$ 1730 cm^{-1} (–CF=CH–), *m*/*e* 265 (M^+), 246 ($C_5HF_9N^+$), 177 ($C_4HF_6N^+$), and 158 ($C_4HF_5N^+$).

Oxidation of both (II) and (III) (2·0 g) with potassium permanganate (1·5 g) in acetone (200 cm^3) at 20° afforded as previously described[24] *S*-benzylisothiouronium trifluoroacetate, (0·8 g) and (0·6 g) respectively, m.p. 172—173° (lit.,[5] 171—173°) (Found: C, 42·5; H, 4·3; N, 10·1. Calc. for $C_{16}H_{11}F_3N_2O_2S$: C, 42·8; H, 4·0; N, 10·0%).

Fraction 2 (b.p. 45—53°, 26·9 g). Separation by g.l.c. (Unit A) in two portions afforded (i) undecafluoro-2-azahex-2-ene (I) (1·95 g), (ii) the *E* and *Z*-isomers (in the ratio 1 : 1) of 1-bistrifluoromethylamino-2*H*-tetrafluoroprop-1-ene (II) and (III) (3·1 g), and (iii) (Z)-5H-*decafluoro-2-azahex-2-ene* (IV) (16·8 g), b.p. 58° (Found: C, 22·7; H, 1·1; F, 71·6. $C_5HF_{10}N$ requires C, 22·6; H, 0·4; F, 71·7%), $\nu_{max.}$ 1770 cm^{-1} (–CF=N–), *m*/*e* 265 (M^+), 164 ($C_3F_6N^+$), 159 ($C_4H_5N^+$), 127 ($C_3HF_4N^+$), 111 ($C_2F_4N^+$), 95 ($C_2F_3N^+$), and 83 (CF_3N^+).

Fraction 3 (b.p. 53—62°, 29·1 g). This was shown by i.r. spectroscopy to be essentially pure 5*H*-decafluoro-2-azahex-2-ene (IV).

Fraction 4 (b.p. 62—71°, 28·2 g). Separation of a portion (2 g) by repeated injections into Unit B at 50° gave three components in the ratio 3 : 7 : 10; (i) a component not identified, (ii) (2Z,4E)-4H,5H-*heptafluoro-2-azahexa*-2,4-*diene* (V), b.p. 73° (Found: C, 28·5; H, 1·0; F, 63·4. $C_5H_2F_7N$ requires C, 28·7; H, 1·0; F, 63·6%), $\nu_{max.}$ 1670 (–CH=CH–) and 1730 cm^{-1} (CF=N–), *m*/*e* 209 (M^+), 190 ($C_5H_2F_6N^+$), 159 ($C_4H_2F_5N^+$), 140 ($C_4H_2F_4N^+$), 120 ($C_4HF_3N^+$), and 95 ($C_2F_3N^+$), and (iii) (2Z,4Z)-5H-*octafluoro-2-azahexa-2,4-diene* (VI), b.p. 77·5° (Found: C, 26·7; F, 66·7. C_5HF_8N requires C, 26·4; F, 67·0%), $\nu_{max.}$ 1690 (CF=CH–) and 1740 cm^{-1} (–CF=N–), *m*/*e* 227 (M^+), 208 ($C_5HF_7N^+$), 158 ($C_4HF_5N^+$), 113 ($C_3HF_4^+$), 94 ($C_3HF_3^+$), and 93 ($C_3F_3^+$).

Fraction 5 (b.p. 71—72·5°, 46·2 g). This was a mixture of two components, in the ratio 7 : 12 by peak areas and was shown by small scale separation and i.r. spectroscopic comparison to be compounds (V) and (VI).

Fraction 6 (b.p. 72—75°, 27·5 g). This mixture of four major components was separated by g.l.c. (Unit A) in portions to afford (i) a mixture of two components in ratio 1 : 1 by peak areas (7·7 g) further separated (Unit B) to give (a) (2Z,4Z)-5-*bistrifluoromethylamino-octafluoro*-2-*azahexa*-2,4-*diene* (VIII), b.p. 82—83° (Found: C, 21·6; F, 70·2. $C_7F_{14}N_2$ requires C, 22·2; F, 70·4%), *m*/*e* 378 (M^+), 359 ($C_7F_3N_2^+$), and 309 ($C_6F_4N_2^+$) and (b) (2Z,4E)-5-*bistrifluoromethylamino-octafluoro-2-azahexa*-2,4-*diene* (VII), b.p. 81·5° (Found: C, 22·4; F, 70·3. $C_7F_{14}N_2$ requires C, 22·2; F, 70·4%), *m*/*e* 378 (M^+), 359 ($C_7F_{13}N_2^+$), 309 ($C_6F_{11}N_2^+$), 290 ($C_6F_{10}N_2^+$), 271 ($C_6F_9N_2^+$), and 114

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1973, Index issue.

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($C_2F_4N^+$); (ii) compound (VI) (8·0 g); and (iii) 1-*difluoromethyl*-3H-*heptafluoropyrrolidine* (IX) (4·6 g), b.p. 77—79° (Found: C, 24·6; H, 0·6; F, 69·0. $C_5H_2F_9N$ requires: C, 24·3; H, 0·8; F, 69·2%), *m/e* 247 (M^+), 228 ($C_5H_2F_8N^+$), 209 ($C_5H_2F_7N^+$), 178 ($C_4H_2F_6N^+$), and 158 ($C_4HF_5N^+$).

Fluorination of 4-Methylpyridine.—In the same way as described for pyridine above, 4-methylpyridine was fluorinated at 200—220°. In a typical run, 100 g of the pyridine yielded 70 g of product, b.p. >20°. Analytical g.l.c. indicated a complex mixture of products containing four major components. Fractionation as before of 204 g of the mixture gave three fractions, 1, b.p. <65°, 66·8 g; 2, b.p. 65—85°, 68·8 g; and 3, b.p. 85—95°, 31·1 g; pot residue 30·3 g. A portion of fraction 1 was separated into its major components in a qualitative manner to give (i) (Z)-5-*trifluoromethyldecafluoro*-2-*azahex*-2-*ene* (X), b.p. 62·5° (Found: C, 21·4; F, 74·6. $C_6F_{13}N$ requires C, 21·6; F, 74·2%), $\nu_{max.}$ 1770 cm^{-1} (–CF=N–), *m/e* 333 (M^+), 314 ($C_6F_{12}N^+$), 226 ($C_5F_7N^+$), 181 ($C_4F_7^+$), 145 ($C_3F_5N^+$), and 114 ($C_2F_4N^+$), and (ii) (Z)-5-*trifluoromethyloctafluoro*-2-*azahexa*-2,4-*diene* (XI), b.p. 65° (Found: C, 24·2; F, 70·4. $C_6F_{11}N$ requires C, 24·4; F, 70·9%), $\nu_{max.}$ 1700 (–CF=C) and 1770 cm^{-1} (CF=N–), *m/e* 295 (M^+), 276 ($C_6F_{10}N^+$), 188 ($C_5F_6N^+$), 181 ($C_4F_7^+$), 150 ($C_3F_6^+$), and 114 ($C_2F_4N^+$). Similarly a portion of fraction 2 gave (i) compound (XI); (ii) (Z)-5-*methyldecafluoro*-2-*azahex*-2-*ene* (XII), b.p. 76·5° (Found: C, 25·9; H, 0·8; F, 68·5; N, 5·3. $C_6H_3F_{10}N$ requires C, 25·8; H, 1·1; F, 68·1; N, 5·6%), $\nu_{max.}$ 1770 cm^{-1} (–CF=N–), *m/e* 260 ($M - 19$), 165 ($C_4H_3F_6^+$), 145 ($C_4H_2F_5^+$), 115 ($C_3H_3F_6^+$), and 114 ($C_2F_4N^+$); and (iii) (Z)-5-*difluoromethyldecafluoro*-2-*azahex*-2-*ene* (XIII), b.p. 79·5° (Found: C, 22·8; H, 6·9; F, 72·7; N, 4·0. $C_6H_2F_{11}N$ requires C, 22·8; H, 0·3; F, 72·4; N, 4·5%), $\nu_{max.}$ 1775 cm^{-1} (–CF=N–), *m/e* 296 ($M - 19$), 246 ($C_5HF_9N^+$), 164 ($C_3F_6N^+$), and 114 ($C_2F_4N^+$).

[4/082 *Received, 17th January,* 1974]