

## *N*-Halogeno-compounds. Part 3.<sup>1</sup> *N*-Chlorination of Some Fluorinated Aryl- and Heteroaryl-amines and Anilides

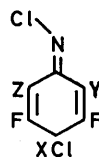
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*t*-Butyl hypochlorite has been used to convert 4-aminoheptafluorotoluene, 4-amino-2,3,5,6-tetrafluorobiphenyl, chlorotetrafluoroanilines, 4-amino-3-chlorotrifluoropyridine, and 4-aminotrifluoropyrimidine into the corresponding *NN*-dichloro-amines; *N*-methylpentafluoroaniline, tetrafluoro-4-(methylamino)pyridine, 3,5-dichloro-2,6-difluoro-4-(methylamino)pyridine, pentafluoroacetanilide, and pentafluorotrifluoroacetanilide into the corresponding *N*-monochloro-compounds; and 4,4'-diamino-octafluorobiphenyl into the corresponding bis(dichloro-amino)-compound. Treatment of 2,3,4,5-tetrafluoroaniline with *t*-butyl hypochlorite gave *N*,4-dichloro-2,3,4,5-tetrafluorocyclohexa-2,5-dienylideneamine and 2*H*,2'*H*-octafluoroazobenzene. Perfluoro-(4,4'-dimethylazobenzene) and 2,2',3,3',5,5',6,6'-octafluoro-4,4'-diphenylazobenzene were procured by thermolysis of the appropriate *NN*-dichloro-amines. Analysis of the <sup>19</sup>F n.m.r. spectra of the dichloro-amines has enabled the electronic effect of the NCl<sub>2</sub> group to be assessed.

ONLY four aromatic *NN*-dichloro-amines [(1),<sup>2</sup> (2),<sup>3</sup> (3),<sup>4</sup> and (4)<sup>5</sup>] stable enough to allow their properties to be examined in comfort appear to have been isolated since Goldschmidt commenced his classical studies on the action of hypochlorites on arylamines more than 60 years ago.<sup>6</sup> We now report the synthesis of seven more [(5)–(11)], including the first belonging to the pyrimidine class (5) and the first bis(dichloroamino)-compound (6). Financial factors determined the reactions studied: samples of either the amines to be chlorinated or their immediate precursors had to be available through our earlier researches or those of colleagues.

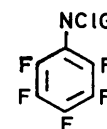
Electrophilic chlorination of 4-amino-2,3,5,6-tetrafluorobiphenyl [→ (9) (94%)], 4-aminoheptafluorotoluene [→ (8) (65%)], a *ca.* 25 : 5 : 70 mixture of per-

and 4,4'-diamino-octafluorobiphenyl [→ (6) (81%)] with *t*-butyl hypochlorite in carbon tetrachloride or chloroform (or mixtures of these) occurred smoothly. The products (9) and (6) were pale yellow solids, and the

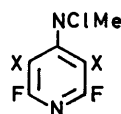


(13) X = Y = F, Z = H

(14) Z = F, X and Y as in (8)–(11)

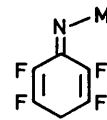


(15) G = Me

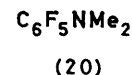
(16) G = COMe or COCF<sub>3</sub>

(17) X = F

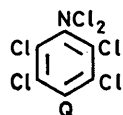
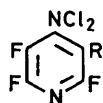
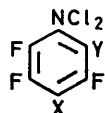
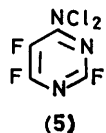
(18) X = Cl



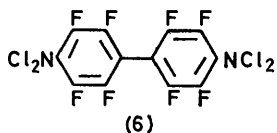
(19)



(20)

(1) Q = Cl  
(2) Q = OH(3) R = F  
(7) R = Cl(4) X = Y = F  
(8) X = CF<sub>3</sub>, Y = F  
(9) X = Ph, Y = F  
(10) X = F, Y = Cl  
(11) X = Cl, Y = F  
(12) X = F, Y = H

(5)



(6)

fluoro-*o*-, *m*-, and *p*-chloroaniline [→ (10) and (11) (70%); no *m*-isomer detected by <sup>19</sup>F n.m.r. spectroscopy], 4-amino-3-chlorotrifluoropyridine [→ (7) (58%)], 4-aminotrifluoropyrimidine [→ (5) (57%)],

others were yellow pungent-smelling liquids; they all rapidly oxidized iodide to iodine (KI in wet Me<sub>2</sub>CO), and none appeared to decompose during several days at room temperature in the dark.

'Spontaneous' isomerization of the *NN*-dichloro-aniline derivatives (8)–(11) to cyclohexadienylideneamines was not encountered (*cf.* our experience with *NN*-dichloropentafluoroaniline<sup>5</sup>), but attempts to isolate 1-(dichloroamino)-2,3,4,5-tetrafluorobenzene (12) following treatment of 2,3,4,5-tetrafluoroaniline with *t*-butyl hypochlorite at –15 to 20 °C resulted in exothermic formation of *N*,4-dichloro-2,3,4,5-tetrafluorocyclohexa-2,5-dienylideneamine (13) plus the known 2*H*,2'*H*-octafluoroazobenzene. Iodine-initiated<sup>5</sup> isomerization of the *NN*-dichloro-amines (8)–(11) to the corresponding *N*-chloro-imines (14) proceeded smoothly at room temperature.<sup>1</sup> As expected,<sup>2,4,5</sup> thermolysis of compounds

<sup>1</sup> Part 2, R. E. Banks, M. G. Barlow, and T. J. Noakes, *J. Fluorine Chem.*, in the press.

<sup>2</sup> S. Goldschmidt and L. Strohmenger, *Ber.*, 1922, **55**, 2450.

<sup>3</sup> W. Eller and L. Klemm, *Ber.*, 1922, **55**, 217.

<sup>4</sup> R. E. Banks and T. J. Noakes, *J.C.S. Perkin I*, 1975, 1419.

<sup>5</sup> R. E. Banks and T. J. Noakes, *J.C.S. Perkin I*, 1976, 143.

<sup>6</sup> For reviews dealing with *N*-halogenation of arylamines, see 'A Shorter Sidgwick's Organic Chemistry of Nitrogen' (prepared by I. T. Millar and H. D. Springhall), Oxford University Press, 1969, p. 101, and B. C. Challis and A. R. Butler in 'The Chemistry of the Amino Group', ed. S. Patai, Wiley-Interscience, London, 1968, p. 302.

(8) and (9) provided the azo-compounds  $4\text{-F}_3\text{C}\cdot\text{C}_6\text{F}_4\cdot\text{N}:\text{N}\cdot\text{C}_6\text{F}_4\cdot\text{CF}_3\text{-4}'$  and  $4\text{-PhC}_6\text{F}_4\cdot\text{N}:\text{N}\cdot\text{C}_6\text{F}_4\text{Ph-4}'$ , respectively; a single attempt to convert the bis(dichloroamino)-compound (6) into the azo-polymer  $[\text{C}_6\text{F}_4\cdot\text{C}_6\text{F}_4\cdot\text{N}:\text{N}]_n$  by heating it in boiling carbon tetrachloride gave a multi-component (six or more by t.l.c.) bright red solid (m.p.  $>300^\circ\text{C}$ ), elemental analysis of which revealed that only about half the chlorine available in the monomer had been evolved.

*t*-Butyl hypochlorite in carbon tetrachloride and/or chloroform has also been employed to prepare the first

respect to the coupled fluorines, *ortho,ortho*, *ortho,para*, or *meta,meta*, for four-bond couplings. For  $\text{NMe}_2$  this leads to the contributions *o,o* +2.1, *o,p* -4.1, and *m,m* -1.7 Hz, and for  $\text{NCl}_2$  *o,o* -7.1, *o,p* +2.5, and *m,m* -0.2 Hz if the tentative signs suggested by the chemical shift correlations are accepted. The contributions for  $\text{NClMe}$  fall between these.

Consideration of the Hammett  $\sigma_p$  value for  $\text{NMe}_2$ <sup>9</sup> (-0.83) leads to a predicted *o,o* contribution of about 9 Hz. The observed value (+2.1 Hz) correlates with  $\sigma_p$  ca. -0.2, implying that the substituent is not perturb-

<sup>19</sup>F N.m.r. parameters

Compound	Chemical shifts (p.p.m.) <sup>a</sup>			Coupling constants (Hz) <sup>b</sup>					
	$\delta_{2,6}$	$\delta_{3,5}$	$\delta_4$	$J_{2,3}$	$J_{2,4}$	$J_{2,5}$	$J_{2,6}$	$J_{3,4}$	$J_{3,5}$
(20) <sup>c</sup>	73.6	87.1	88.1	-20.9	-2.5	5.4	0.0	-21.4	-3.6
(15) <sup>d,e</sup>	69.5	89.0	81.5	-20.4	(-1.8)	6.3	(-5.7)	-20.2	(-2.7)
(4) <sup>d</sup>	66.6	86.0	75.4	-20.7	(+4.1)	6.8	(-9.2)	-20.5	(-2.1)
(3) <sup>d</sup>	9.8	65.4		-19.5		28.7	14.1		(-6.1)

<sup>a</sup> To high field of  $\text{CF}_3\cdot\text{CO}_2\text{H}$ . <sup>b</sup> The *ortho*-coupling is assumed to be negative (L. Snyder and E. W. Anderson, *J. Chem. Phys.*, 1965, **42**, 3336) and the signs in parentheses are only tentative. <sup>c</sup> In  $\text{CCl}_4$  (25% v/v), and analysed at 56.46 and 94.1 MHz as an AA'BBX' system in which the nuclei X are further perturbed by first-order coupling to the substituent protons (1.9 Hz). <sup>d</sup> Neat liquids, analysed as AA'XX' or AA'PXX' systems. <sup>e</sup>  $J_{2,H}$  1.3 Hz.

*N*-monochloro-arylamines [(15), (17), and (18)] and *N*-chloroacetanilides (16) of the fluorocarbon class from the corresponding *N*-H compounds. Iodine-initiated rearrangement of *N*-chloro-*N*-methylpentafluoroaniline (15) to a 4-chlorocyclohexa-2,5-dienylideneamine (19)<sup>1</sup> occurs noticeably more reluctantly than the corresponding isomerization of any *NN*-dichloroaniline studied so far; this is not inconsistent with the mechanism postulated previously.<sup>5</sup>

<sup>19</sup>F *N.m.r.* Parameters and the Electronic Effect of the  $\text{NCl}_2$  Group.—Chemical shifts and coupling constants for the pentafluorobenzenes  $\text{C}_6\text{F}_5\text{NMe}_2$  (20),  $\text{C}_6\text{F}_5\text{NClMe}$  (15), and  $\text{C}_6\text{F}_5\text{NCl}_2$  (4), and for 4-(dichloroamino)tetrafluoropyridine (3) are listed in the Table.

The effects of substituents on the four-bond coupling constants involving *meta*-fluorine nuclei in fluorobenzenes, and the five-bond couplings, are constant.<sup>7</sup> Furthermore, a linear correlation exists between the chemical shift of the 4-fluorine nucleus and the values of  $J_{2,6}$  and  $J_{2,4}$  in a pentafluorobenzene;<sup>8</sup> both types of correlation appear to reflect the influence exerted by a substituent on the  $\pi$ -electronic distribution. Since the spatial demands of the substituents  $\text{NMe}_2$ ,  $\text{NClMe}$ , and  $\text{NCl}_2$  ought to be similar, it should therefore be possible to throw light on the electronic character of the  $\text{NCl}_2$  group by consideration of the differences in the n.m.r. parameters of compounds (20), (15), and (4).

The approach used by Abraham *et al.*<sup>7</sup> is to assign a contribution to the experimental coupling constant which depends on the orientation of the substituent with

\* That *N*-methyl-*ortho*-fluorine interaction bends or twists the  $\text{NMe}_2$  group out of the plane of the ring in  $\text{C}_6\text{F}_5\text{NMe}_2$  was postulated previously on the basis of u.v. spectral data and the *meta:para* ratio (ca. 0.07:1) for nucleophilic attack on the system.<sup>10</sup>

<sup>7</sup> R. J. Abraham, D. B. Macdonald, and E. S. Pepper, *J. Amer. Chem. Soc.*, 1968, **90**, 147.

ing the  $\pi$ -electrons as much as expected—a situation consonant with steric inhibition of resonance owing to interference between the methyl groups and the *ortho*-fluorine atoms.\* The values for the  $\text{NCl}_2$  substituent are clearly those of an electron-withdrawing group, *o,o* -7.1 Hz being consistent with a  $\sigma_p$  value of +0.65, close to that for a  $\text{C}\equiv\text{N}$  group; the  $\text{NCl}_2$  group must surely be twisted well out of the plane of the ring, a deduction supported by a Courtauld molecular model.

A similar approach can be used with the pyridine derivative (3), the ring nitrogen atom being treated like a substituent in a benzene system.<sup>11</sup> The values for  $\text{NCl}_2$  lead to a predicted  $J_{3,5}$  value of -6.6 Hz, with one of the *meta*-coupling constants 6.1 Hz and the other 14.1 Hz. The assignments in the Table follow.

In 4-substituted trifluoropyrimidines the small *meta*-coupling  $J_{2,6}$  is unmeasurable owing to quadrupolar broadening by the adjacent nitrogen nuclei.<sup>12</sup> When the substituent is  $\text{NCl}_2$ , quadrupolar relaxation seems to be fairly rapid and a coupling constant of magnitude 2.6 Hz is observed.

#### EXPERIMENTAL

*N.m.r. Spectroscopy.*—<sup>19</sup>F and <sup>1</sup>H chemical shifts were measured relative to external  $\text{CF}_3\cdot\text{CO}_2\text{H}$  (upfield shifts designated positive) and, unless stated otherwise,  $\text{Me}_4\text{Si}$  (downfield shifts positive), respectively.

2,3,5,6-Tetrafluoro-4-(methylamino)pyridine.—The precipitate obtained when a mixture of aqueous 30% w/v methylamine (4.5 cm<sup>3</sup>) and ethanol (3 cm<sup>3</sup>) was added

<sup>8</sup> M. G. Hogben and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1969, **91**, 283.

<sup>9</sup> D. H. MacDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

<sup>10</sup> J. G. Allen, J. Burdon, and J. C. Tatlow, *J. Chem. Soc.*, 1965, 6329.

<sup>11</sup> J. W. Emsley and L. Phillips, *J. Chem. Soc. (B)*, 1969, 434.

<sup>12</sup> R. E. Banks, D. S. Field, and R. N. Haszeldine, *J. Chem. Soc. (C)*, 1967, 1822.

dropwise to a cold (0 °C) stirred solution of pentafluoropyridine (3.0 g, 17.8 mmol) in ethanol (3 cm<sup>3</sup>) was crystallized from light petroleum (b.p. 60–80 °C) to provide needles of 2,3,5,6-tetrafluoro-4-(methylamino)pyridine (1.6 g, 8.9 mmol, 50%) (Found: C, 39.9; H, 2.3; N, 15.6. C<sub>8</sub>H<sub>4</sub>F<sub>4</sub>N<sub>2</sub> requires C, 40.0; H, 2.2; N, 15.6%), m.p. 88–89 °C,  $\delta_F$  (84.6 MHz; CDCl<sub>3</sub>) 16.9 (2-, 6-F) and 86.9 p.p.m. (3-, 5-F),  $\delta_H$  (90 MHz; CDCl<sub>3</sub>) 3.27 (Me,  $^1J_{H,F}$  2.6,  $|J_{H,H}|$  5.2 Hz), and 4.8br p.p.m. (NH).

3,5-Dichloro-2,6-difluoro-4-(methylamino)pyridine.— The above experiment was repeated with 3,5-dichlorotrifluoropyridine, to provide 3,5-dichloro-2,6-difluoro-4-(methylamino)pyridine (69%) (Found: C, 34.0; H, 2.0; N, 13.2. C<sub>8</sub>H<sub>4</sub>Cl<sub>2</sub>F<sub>2</sub>N<sub>2</sub> requires C, 33.8; H, 1.9; N, 13.15%), m.p. 107–108 °C,  $\delta_F$  (84.6 MHz; 30% w/v in CDCl<sub>3</sub>) –4.9 p.p.m. (s),  $\delta_H$  (90 MHz; same soln.) 3.45 (Me,  $|J_{H,H}|$  5.4 Hz) and 5.2br p.p.m. (NH).

Chlorination of Amines.—(a) 4-Aminoheptafluorotoluene. Using the cautious procedure employed in the chlorination of 4-aminotetrafluoropyridine,<sup>4</sup> it was found that a reaction occurs between 4-aminoheptafluorotoluene (5.0 g, 21 mmol) and t-butyl hypochlorite (6.0 g, 55 mmol) in AnalaR carbon tetrachloride (350 cm<sup>3</sup>) at the b.p. of the solvent to yield (after 4 h, work-up as described for NN-dichloropentafluoroaniline<sup>5</sup>) 1-(dichloroamino)-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene (4.1 g, 13.6 mmol, 65%) (Found: C, 27.4; Cl, 24.0; F, 43.0; N, 4.4. C<sub>7</sub>Cl<sub>2</sub>F<sub>7</sub>N requires C, 27.8; Cl, 23.5; F, 44.0; N, 4.6%), a lemon-yellow liquid, m.p. ca. –14 °C,  $\delta_F$  (56.46 MHz) –19.8 (CF<sub>3</sub>, t, 22.0 Hz) and ca. 62.1 and 63.5 p.p.m. (ring Fs; complex, ill-resolved, AA'BB' sub-spectrum).

(b) 4-Amino-2,3,5,6-tetrafluorobiphenyl. The pale yellow solid formed when a cold (ca. –15 °C) solution of 4-amino-2,3,5,6-tetrafluorobiphenyl (4.0 g, 17 mmol) and t-butyl hypochlorite (3.8 g, 35 mmol) in AnalaR carbon tetrachloride (300 cm<sup>3</sup>) was stirred for 30 min was washed with carbon tetrachloride then dried *in vacuo* to provide 4-(dichloroamino)-2,3,5,6-tetrafluorobiphenyl (5.0 g, 16 mmol, 94%) (Found: C, 46.4; H, 1.7; Cl, 22.3; F, 24.9; N, 4.3. C<sub>12</sub>H<sub>5</sub>Cl<sub>2</sub>F<sub>4</sub>N requires C, 46.45; H, 1.7; Cl, 22.9; F, 24.5; N, 4.5%).

(c) Chlorotetrafluoroanilines. AnalaR carbon tetrachloride (75 cm<sup>3</sup>) containing a ca. 25 : 5 : 70 mixture of perfluoro-*o*-, *m*-, and *p*-chloroaniline (from <sup>13</sup>C<sub>6</sub>F<sub>5</sub>Cl and ethanolic NH<sub>3</sub> aq. at 157 °C) (6.0 g, 30 mmol) was added slowly to a cold (ca. –15 °C) stirred solution of t-butyl hypochlorite (6.9 g, 63 mmol) in AnalaR carbon tetrachloride (100 cm<sup>3</sup>). A reaction occurred only when the mixture was allowed to warm to room temperature (i.r. spectroscopy was used to detect consumption of the anilines), and immediate work-up as in (a) gave a pale yellow liquid mixture (ca. 1 : 3 by <sup>19</sup>F n.m.r. spectroscopy) of 1-chloro-2-(dichloroamino)- and 1-chloro-4-(dichloroamino)-tetrafluorobenzene (5.6 g, 21 mmol, 70%) (Found: C, 27.9; Cl, 39.5; F, 29.0; N, 4.5. Calc. for C<sub>6</sub>Cl<sub>3</sub>F<sub>4</sub>N: C, 26.8; Cl, 39.7; F, 28.3; N, 5.2%),  $\delta_F$  (56.46 MHz) 60, 72, and 77 p.p.m. (2 : 1 : 1) [2-(dichloroamino)-compound], and 60.5 and 62 p.p.m. (1 : 1) [4-(dichloroamino)-compound].

(d) 2,3,4,5-Tetrafluoroaniline. A mixture of the amine (10.0 g, 60.6 mmol) and t-butyl hypochlorite (13.2 g, 122 mmol) in cold (ca. –15 °C) AnalaR carbon tetrachloride (250 cm<sup>3</sup>) was stirred for 30 min, warmed to 20 °C, then evaporated *in vacuo*. The residual yellow oil suddenly

darkened in colour, became hot, and evolved a gas that smelled like chlorine and bleached damp litmus paper. Short-path distillation of the final product provided *N*,4-dichloro-2,3,4,5-tetrafluorocyclohexa-2,5-dienylideneamine (6.2 g, 26.5 mmol, 43%), and recrystallization of the distillation residue from light petroleum (b.p. 60–80 °C) afforded 2*H*,2'*H*-octafluoroazobenzene<sup>14</sup> (1.0 g, 3.1 mmol, 10%), both products being identified spectroscopically (i.r. and n.m.r.).

The experiment was repeated, but after the cold reaction mixture had been stirred for 30 min a small crystal of iodine was added. Distillation of the mixture then provided *N*,4-dichloro-2,3,4,5-tetrafluorocyclohexa-2,5-dienylideneamine (11.3 g, 48.3 mmol, 80%) (Found: C, 30.8; H, 0.6; Cl, 30.3; F, 32.3; N, 5.8. C<sub>6</sub>HCl<sub>2</sub>F<sub>4</sub>N requires C, 30.8; H, 0.4; Cl, 30.3; F, 32.5; N, 6.0%), a pale yellow, sweet-smelling oil,  $\lambda_{max}$  (film) 3.23m (C–H str.), 5.81m (CF=CF str.), and 6.02s  $\mu$ m (CH=CF str.),  $\lambda_{max}$  (hexane) 263 nm ( $\epsilon$  19 500) (<sup>19</sup>F n.m.r. parameters discussed elsewhere<sup>1</sup>).

(e) *N*-Methylpentafluoroaniline. A stirred solution of the amine (10.0 g, 50.8 mmol) and t-butyl hypochlorite (6.5 g, 60 mmol) in AnalaR carbon tetrachloride (250 cm<sup>3</sup>) was prepared at –15 °C, stored at that temperature for 1 h, then worked up by the method used to isolate NN-dichloropentafluoroaniline,<sup>5</sup> to provide *N*-chloro-2,3,4,5,6-pentafluoro(methylamino)benzene (8.1 g, 35 mmol, 69%) (Found: C, 36.1; H, 1.4; Cl, 15.8; F, 40.8; N, 5.9. C<sub>7</sub>H<sub>3</sub>ClF<sub>5</sub>N requires C, 36.3; H, 1.3; Cl, 15.3; F, 41.0; N, 6.0%), a pale yellow oil that rapidly oxidised potassium iodide in wet acetone to iodine.

(f) 4,4'-Diamino-octafluorobiphenyl. A solution of the diamine (10.0 g, 30.5 mmol) in AnalaR chloroform (200 cm<sup>3</sup>) was added dropwise to a cold (ca. –15 °C) stirred solution of t-butyl hypochlorite (13.0 g, 120 mmol) in AnalaR carbon tetrachloride (200 cm<sup>3</sup>). The mixture was warmed to 20 °C then evaporated at water-pump pressure until precipitation of a pale yellow solid was complete; the solid was dried *in vacuo* and shown to be 4,4'-bis(dichloroamino)octafluorobiphenyl (11.5 g, 24.7 mmol, 81%) (Found: C, 31.0; Cl, 30.7; F, 32.2; N, 6.0. C<sub>12</sub>Cl<sub>4</sub>F<sub>8</sub>N<sub>2</sub> requires C, 30.9; Cl, 30.5; F, 32.6; N, 6.0%), which oxidized potassium iodide in wet acetone to iodine;  $\delta_F$  (56.46 MHz; CCl<sub>4</sub>) 59 (3-, 3'-, 5-, 5'-F) and 64 p.p.m. (2-, 2'-, 6-, 6'-F) (broad, complex, ill-defined bands).

(g) 4-Amino-3-chloro-2,5,6-trifluoropyridine. No reaction appeared to occur between this amine and t-butyl hypochlorite in AnalaR chloroform at temperatures below 40 °C. Chlorination occurred only slowly at 50 °C, and distillation (as described previously<sup>4</sup>) of the product obtained by heating under reflux for 12 h a solution of the amine (2.0 g, 11 mmol) and t-butyl hypochlorite (3.0 g, 28 mmol) in chloroform (80 cm<sup>3</sup>) gave 3-chloro-4-(dichloroamino)-2,5,6-trifluoropyridine (1.6 g, 6.4 mmol, 58%) (Found: C, 24.0; F, 23.0; N, 11.2. C<sub>5</sub>Cl<sub>3</sub>F<sub>3</sub>N<sub>2</sub> requires C, 23.9; F, 22.7; N, 11.1%), an amber, pungent-smelling oil containing 'positive' chlorine (KI in wet Me<sub>2</sub>CO test),  $\delta_F$  (94.1 MHz; 40% w/v in CCl<sub>4</sub>) –8.0 (2-F;  $|J_{2,5}|$  28.5,  $|J_{2,6}|$  13.5 Hz), 6.7 (6-F;  $|J_{5,6}|$  20.4 Hz), and 63.1 p.p.m. (5-F); the methods of Emsley and Phillips<sup>11</sup> lead to a calculated  $J_{2,6}$  value of 12.3 Hz.

(h) 2,3,5,6-Tetrafluoro-4-(methylamino)pyridine. A solution of the amine (0.8 g, 4.4 mmol) and t-butyl hypochlorite

<sup>13</sup> G. M. Brooke, R. D. Chambers, J. Heyes, and W. K. R. Musgrave, *Proc. Chem. Soc.*, 1963, 213.

<sup>14</sup> J. M. Birchall, R. N. Haszeldine, and J. E. G. Kemp, *J. Chem. Soc. (C)*, 1970, 449.

(0.7 g, 6.5 mmol) in AnalaR carbon tetrachloride (16 cm<sup>3</sup>) was heated under reflux for 5 h then evaporated at 10 °C and *ca.* 0.2 mmHg. Short-path distillation of the oily residue at 50 °C *in vacuo* provided 4-(*N*-chloromethylamino)-2,3,5,6-tetrafluoropyridine (0.5 g, 2.3 mmol, 52%) (Found: C, 33.7; H, 1.6; N, 12.9. C<sub>6</sub>H<sub>3</sub>ClF<sub>4</sub>N<sub>2</sub> requires C, 33.6; H, 1.4; N, 13.05%),  $\delta_F$  (84.6 MHz; neat liq.) 13.5 (2-, 6-F) and 69.0 p.p.m. (3-, 5-F),  $\delta_H$  (90 MHz) 3.35 (upfield from ext. *p*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>), as a lemon-yellow oil.

(i) 3,5-Dichloro-2,6-difluoro-4-(methylamino)pyridine. Experiment (h) was repeated with this amine (4.0 g, 19 mmol) and *t*-butyl hypochlorite (2.9 g, 17 mmol) in boiling AnalaR carbon tetrachloride (60 cm<sup>3</sup>) for 10 h, to provide pale yellow 4-(*N*-chloromethylamino)-3,5-dichloro-2,6-difluoropyridine (4.2 g, 17 mmol, 89%) (Found: C, 29.3; H, 1.2; N, 11.1. C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub>F<sub>2</sub>N<sub>2</sub> requires C, 29.1; H, 1.2; N, 11.3%), m.p. 42 °C [from light petroleum (b.p. 30–40 °C)],  $\delta_F$  (84.6 MHz; 30% w/v in CCl<sub>4</sub>) –9.1 p.p.m.,  $\delta_H$  3.42, which contained 'positive' chlorine (KI in wet Me<sub>2</sub>CO test).

(j) 4-Amino-2,5,6-trifluoropyrimidine. The method used to obtain 4-(dichloroamino)tetrafluoropyridine<sup>4</sup> was applied to 4-aminotrifluoropyrimidine (7.0 g) to provide 4-(dichloroamino)-2,5,6-trifluoropyrimidine (5.8 g, 57%) (Found: C, 22.2; Cl, 33.4; F, 25.4; N, 19.0. C<sub>4</sub>Cl<sub>2</sub>F<sub>3</sub>N<sub>3</sub> requires C, 22.0; Cl, 32.6; F, 26.1; N, 19.3%),  $\delta_F$  (56.46 MHz; neat liq.) –32.0 (2-F;  $|J_{2,6}|$  2.6,  $|J_{2,5}|$  27.0 Hz), –3.0 (6-F;  $|J_{5,6}|$  18.3 Hz), and 77.0 p.p.m. (5-F), a pale yellow oil isolated by the method used for *NN*-dichloropentafluoroaniline.<sup>5</sup>

*Chlorination of Anilides.*—(a) 2,3,4,5,6-Pentafluoroacetanilide. A solution of pentafluoroacetanilide (4.0 g, 18 mmol) and *t*-butyl hypochlorite (2.0 g, 18 mmol) in chloroform (60 cm<sup>3</sup>) and carbon tetrachloride (50 cm<sup>3</sup>) was heated under reflux for 4 h (no reaction appeared to occur at temperatures up to 30 °C, as established by i.r. analysis of samples at intervals as the temperature was raised to that value from –10 °C). The product was evaporated at *ca.* 15 °C and 0.2 mmHg, then the residue was subjected to short-path distillation at 30 °C *in vacuo* to provide *N*-chloro-2,3,4,5,6-pentafluoroacetanilide (3.2 g, 12 mmol, 67%) (Found: C, 37.3; H, 1.4; F, 36.7; N, 5.4. C<sub>8</sub>H<sub>3</sub>ClF<sub>5</sub>NO requires C, 37.0; H, 1.2; F, 36.6; N, 5.4%), a pale yellow oil,  $\delta_F$  (94.1 MHz; neat liq.) 67.0 (2-, 6-F), 74.1 and 76.0 (4-F), and 84.7 and 86.0 p.p.m. (3-, 5-F) [all the absorption band systems were broad and showed little fine structure; the non-equivalence of the *m*- and *p*-fluorine nuclei is ascribed to the presence of two conformers [in the ratio of

55:45 by integration, the major component causing the lower-field absorption) arising, presumably, from hindered rotation about the C(=O)–N bond]. Iodine (0.359 mmol, 93% of 1 N–Cl link) liberated from potassium iodide in wet acetone by a sample of *N*-chloropentafluoroacetanilide (0.386 mmol) was estimated by titration against sodium thiosulphate.

(b) 2,3,4,5,6-Pentafluorotrifluoroacetanilide. Experiment (a) was repeated with a mixture of pentafluorotrifluoroacetanilide (1.7 g, 6.1 mmol), *t*-butyl hypochlorite (1.0 g, 9.2 mmol), and AnalaR chloroform (10 cm<sup>3</sup>) (reflux period 5 h). Work-up of the pale green product afforded *N*-chloro-2,3,4,5,6-pentafluorotrifluoroacetanilide (1.2 g, 3.8 mmol, 62%) (Found: C, 30.8; Cl, 11.7; F, 48.0. C<sub>8</sub>ClF<sub>8</sub>NO requires C, 30.6; Cl, 11.3; F, 48.5%), a pale green oil,  $\delta_F$  (94.1 MHz) –6.7 (CF<sub>3</sub>), 66.3 (2-, 6-F), 70.8 (4-F), and 84.5 p.p.m. (3-, 5-F) (all the absorptions were broad and displayed little fine structure).

*Preparation of Azo-compounds.*—(a) *Perfluoro*-(4,4'-dimethylazobenzene). A small flask containing 1-(dichloroamino)-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene (1.0 g, 3.3 mmol) and a PTFE-encapsulated stirrer was lowered into a hot (160 °C) oil-bath behind a blast screen; the mixture was stirred for 4 h (excessive). The product was cooled and recrystallized from light petroleum (b.p. 60–80 °C) to provide orange *perfluoro*-(4,4'-dimethylazobenzene) (0.6 g, 1.3 mmol, 79%) (Found: C, 36.2; F, 57.1; N, 6.4. C<sub>14</sub>F<sub>14</sub>N<sub>2</sub> requires C, 36.4; F, 57.5; N, 6.1%), m.p. 122.5–123.5 °C,  $\delta_F$  (56.46 MHz; 15% w/v in Me<sub>2</sub>CO) –20.3 (CF<sub>3</sub>), 64.2 (3-, 3'-, 5-, 5'-F), and 71.8 p.p.m. (2-, 2'-, 6-, 6'-F), *m/e* 462 (*M*<sup>+</sup>, 28), 245 (C<sub>7</sub>F<sub>7</sub>N<sub>2</sub><sup>+</sup>, 25), and 217 (C<sub>7</sub>F<sub>7</sub><sup>+</sup>, 100%).

(b) 2,2',3,3',5,5',6,6'-Octafluoro-4,4'-diphenylazobenzene. A suspension of 4-(dichloroamino)-2,3,5,6-tetrafluorobiphenyl (2.9 g, 9.35 mmol) in light petroleum (b.p. 60–80 °C) was heated vigorously under reflux for 10 min then cooled to 20 °C to provide red needles of 2,2',3,3',5,5',6,6'-octafluoro-4,4'-diphenylazobenzene (0.5 g, 1.05 mmol, 22%) (Found: C, 59.5; H, 2.3; F, 31.0; N, 5.8. C<sub>24</sub>H<sub>10</sub>F<sub>8</sub>N<sub>2</sub> requires C, 60.25; H, 2.1; F, 31.8; N, 5.85%), m.p. 279–281 °C, *m/e* 478 (*M*<sup>+</sup>, 44), 239 (C<sub>12</sub>H<sub>5</sub>F<sub>4</sub>N<sub>2</sub><sup>+</sup>, 47), and 225 (C<sub>12</sub>H<sub>5</sub>F<sub>4</sub><sup>+</sup>, 100%).

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