N-Halogeno-compounds. Part 7.[1] Synthesis and Iodine-catalysed Rearrangement to 6-Chloroimino-1-azacyclohexadienes of 4-Substituted 2-(Dichloroamino)-3,5,6-trifluoropyridines
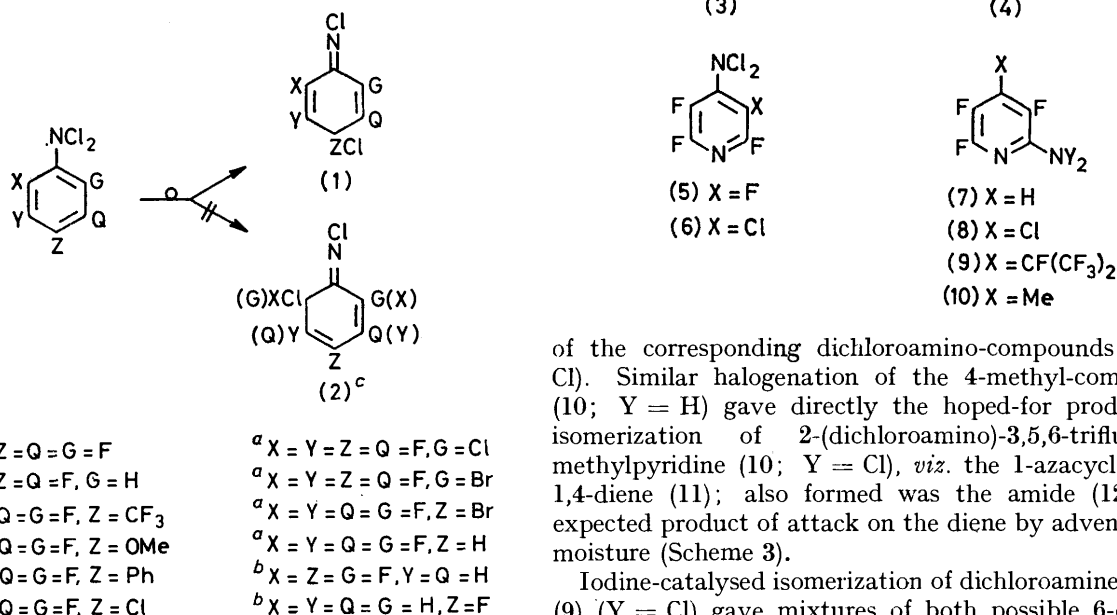
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Electrophilic chlorination of the fluorinated 2-aminopyridines $4\text{-X·C}_5F_3N\text{·NH}_2\text{-2}$ [X = H, Cl, or $CF(CF_3)_2$] with t-butyl hypochlorite gave the 2-(dichloroamino)-compounds $4\text{-X·C}_5F_3N\text{·NCl}_2\text{-2}$; these isomerized to mixtures of the corresponding 3-chloro-6-chloroimino-1-azacyclohexa-1,4- (predominantly) and 5-chloro-6-chloroimino-1-azacyclohexa-1,3-dienes when treated with iodine. 'Spontaneous' formation of 3-chloro-6-chloroimino-2,3,5-trifluoro-4-methyl-1-azacyclohexa-1,4-diene occurred following chlorination (Bu^{t}OCl) of 2-amino-3,5,6-trifluoro-4-methylpyridine. 3-Chloro-6-chloroimino-3,5-difluoro-4-X-2-oxo-1-azacyclohex-4-enes (X = H, Me, or Cl) were obtained by displacement of fluorine from the corresponding 3-chloro-6-chloroimino-2,3,5-trifluoro-1-azacyclohexa-1,4-dienes with water; hydrolysis of 4,5-dichloro-6-chloroimino-2,3,5-trifluoro-1-azacyclohexa-1,3-diene provided 4,5-dichloro-6-chloroimino-3,5-difluoro-2-oxo-1-azacyclohex-3-ene. Pyrolysis of the 2-(dichloroamino)pyridines $4\text{-X·C}_5F_3N\text{·NCl}_2\text{-2}$ [X = Cl or $CF(CF_3)_2$] gave the azo-compounds $2,2'\text{-}[4\text{-X·C}_5F_3\text{-N·N}]_2$. The ^{19}F n.m.r. spectra of the chloroimino-1-azacyclohexadienes have been analysed.

' SPONTANEOUS ' or iodine-catalysed rearrangement of fluorinated NN-dichloroanilines appears to involve only *para*-migration of N-chlorine (Scheme 1),[1-5] whereas exclusive *ortho*-migration [—▸ (3)] seems to occur with perfluoro-2-(dichloroamino)naphthalene;[6] the latter is not unexpected, however, since *para*-migration [—▸ (4)] would entail loss of both Hückel systems. In the pyridine series, compounds (5)[7] and (6)[4] resist isomerization, forcing conditions causing azo-compound formation. Work on electrophilic chlorination of the fluorinated 2-aminopyridines (7)—(10) (Y = H), undertaken to provide aza-analogues of the 2,5-dienes (1) for a study of the skeletal rearrangements which occur when the latter are pyrolysed,[8] has now provided examples where *ortho*-migration of chlorine in monocyclic (dichloro-

amino)arenes [—▸ type (2) isomers] can be detected (Scheme 2).

Chlorination of amines (7)—(9) (Y = H) with t-butyl hypochlorite in carbon tetrachloride (or CCl_4–$CHCl_3$ mixtures) at −16 to 20 °C gave good yields (77—96%)

(*syn*- and *anti*-isomers)

(3)

(4)

(5) X = F
(6) X = Cl

(7) X = H
(8) X = Cl
(9) X = $CF(CF_3)_2$
(10) X = Me

(1)

(2)^c

^{a} X = Y = Z = Q = G = F	^{a} X = Y = Z = Q = F, G = Cl
^{b} X = Y = Z = Q = F, G = H	^{a} X = Y = Z = Q = F, G = Br
^{a} X = Y = Q = G = F, Z = CF$_3$	^{a} X = Y = Q = G = F, Z = Br
^{b} X = Y = Q = G = F, Z = OMe	^{a} X = Y = Q = G = F, Z = H
^{a} X = Y = Q = G = F, Z = Ph	^{b} X = Z = G = F, Y = Q = H
^{a} X = Y = Q = G = F, Z = Cl	^{b} X = Y = Q = G = H, Z = F

SCHEME 1 ^{a} Iodine-catalysed. ^{b} ' Spontaneous ' rearrangement occurs during attempted isolation. ^{c} None detected by ^{19}F n.m.r.

of the corresponding dichloroamino-compounds (Y = Cl). Similar halogenation of the 4-methyl-compound (10; Y = H) gave directly the hoped-for product of isomerization of 2-(dichloroamino)-3,5,6-trifluoro-4-methylpyridine (10; Y = Cl), *viz.* the 1-azacyclohexa-1,4-diene (11); also formed was the amide (12), the expected product of attack on the diene by adventitious moisture (Scheme 3).

Iodine-catalysed isomerization of dichloroamines (7)—(9) (Y = Cl) gave mixtures of both possible 6-chloroimino-1-azacyclohexadienes (Scheme 2); these products also were extremely moisture-sensitive, addition of water to the diene mixture [predominantly (13)] derived from the 4H-compound (7; Y = Cl) and to the major chloro-isomer (15) (isolated by g.l.c.) rapidly giving hydrolysis products (14) and (16) respectively (Scheme 3). A g.l.c.-isolated sample of the minor (1,3-diene)

product of rearrangement of 4-chloro-2-(dichloroamino)-3,5,6-trifluoropyridine (8) hydrolysed to compound (17) when stored in glass.

As expected,[2,4,7] flash pyrolysis of dichloroamines (8)
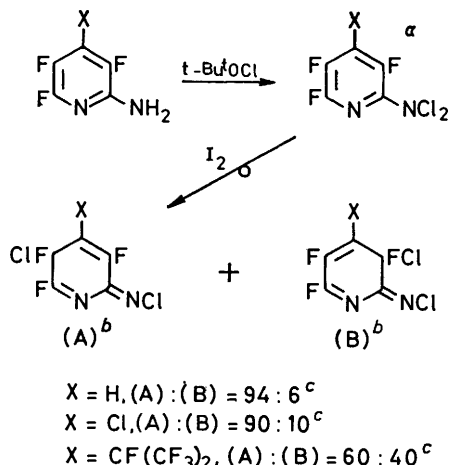
SCHEME 2 [a] Yields: X = H, 96%; X = Cl, 82%; X = CF(CF$_3$)$_2$, 77%. [b] Combined yields [(A) + (B)]: X = H, 86%; X = Cl, 87%; X = CF(CF$_3$)$_2$, 60%. [e] Ratios determined by [19]F n.m.r.

$$X = H, (A):(B) = 94:6 \quad ^c$$
$$X = Cl, (A):(B) = 90:10 \quad ^c$$
$$X = CF(CF_3)_2, (A):(B) = 60:40 \quad ^c$$

and (9) (Y = Cl) provided the corresponding symmetrical azo-compounds, 2,2'-[4-X·C$_5$F$_3$N·N]$_2$.

[19]F *N.m.r. Spectra of Fluorinated 6-Chloroimino-1-azacyclohexadienes.*—Structures were assigned to the rearrangement products of (dichloroamino)pyridines

SCHEME 3

(11) X = Me
(13) X = H
(15) X = Cl

(12) X = Me
(14) X = H
(16) X = Cl
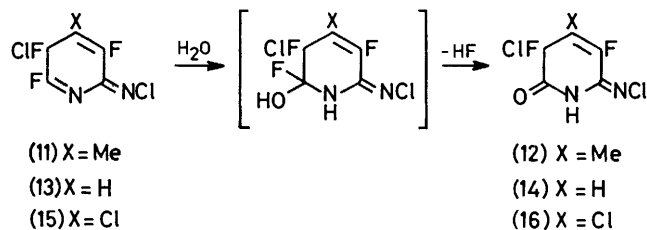
(7)—(10) (Y = Cl) mainly on the basis of [19]F n.m.r. spectroscopic analyses. Parameters obtained by examination of the spectra of the neat mixtures defined in Scheme 2 and of pure samples of the 1,4-dienes (11) and (15) (Scheme 3) are listed in Tables 1 and 2.

(17)
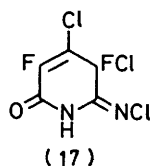
The spectra of all the compounds contained unmistakable [9] low-field absorptions caused by the CF=N groups. The chemical shifts of the fluorines of the CFCl groups in the 1,4-dienes (Table 1) were similar to those observed for the corresponding nuclei in the carbocyclic analogues (1) (−34.6 to −38.2 p.p.m.),[3] although the three-bond couplings |J_{23}| were somewhat larger [25.5—27.2 Hz for

analogues (1) [3]], as are the other coupling constants. In the cases of the 1,3-dienes (Table 2), the magnitudes of the three-bond coupling constants |J_{23}| are close to the value observed in the related azadiene (18); [10] also, the

TABLE 1

[19]F N.m.r. parameters for 6-chloroimino-1-azacyclohexa-1,4-dienes

	Chemical shift (p.p.m.) [a]			Coupling constant (Hz)		
X	δ_2	δ_3	δ_5	|J_{23}|	|J_{25}|	|J_{35}|
Me [b]	27.0	−35.0	−48.4	29	5.5	8.5
H [c]	27.2	−27.0	−42.0	31.3	5.4	8.6
Cl	30.5	−31.5	−41.7	33.0	4.0	7.2
CF(CF$_3$)$_2$ [d]	26.8	−35.5	−25.2	31.5	3.5	8.6

[a] Negative values to high field of external CF$_3$CO$_2$H, and recorded at 84.6 MHz. Neat liquids examined. [b] δ_H (external Me$_4$Si; 60 MHz) 2.0. [c] δ_H (external Me$_4$Si; 90 MHz) 6.49; |J_{2H}| 8.3, |J_{3H}| 5.4, |J_{5H}| 8.3 Hz. [d] δ_{CF_3} 4.1 and 1.5, δ_{CF} −110 p.p.m.

four-bond couplings |J_{35}| compare well with the analogous coupling found with the dienone (19), and the small values of |J_{25}| are consistent with the analogous five-bond coupling constants (1.3—3.5 Hz) reported for related fluorinated cyclohexadienones.[11]
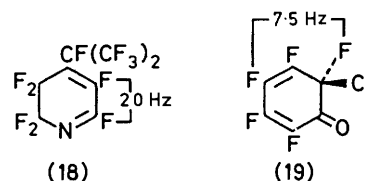
TABLE 2

[19]F N.m.r. parameters for 6-chloroimino-1-azacyclohexa-1,3-dienes

	Chemical shift (p.p.m.) [a]			Coupling constant (Hz)		
X	δ_2	δ_3	δ_5	|J_{23}|	|J_{25}|	|J_{35}|
H [b]	26.4	−51.7	−20.0	23.7	<1	10.5
Cl	27.4	−51.1	−26.0	25.1	<1	8.5
CF(CF$_3$)$_2$ [c]	25.3	−35.5	−33.5	24.2	2.7	10.6

[a] Negative values to high field of external CF$_3$CO$_2$H, and recorded at 84.6 MHz. [b] |J_{2H}| 9.3, |J_{3H}| 7.6, |J_{5H}| 8.5 Hz. [c] δ_{CF_3} 4.5 and 1.2, δ_{CF} −110.1 p.p.m.

The spectrum of the 60 : 40 mixture of the perfluoro-isopropyl compounds (20) and (21) revealed that the two trifluoromethyl groups in each one are non-equivalent, and although some broadening of the absorptions

(18)

(19)

occurred, they did not coalescence at 150 °C. Despite the complexity of the spectrum, it was analysed on a first-order basis to provide the data given in Tables 1 and 2 and structures (20) and (21). The low-field CF$_3$

absorptions are assigned to the groups disposed *syn* to neighbouring chlorine,[12] and the proximity of the tertiary fluorine in each isomer to the fluorine of CFCl is revealed by the large couplings displayed,[13] the magnitudes reflecting a 'through-space' contribution.[14] In the 1,4-diene (20), the difference in the magnitudes of the substantial couplings associated with the CF_3 groups and

(20)   (21)
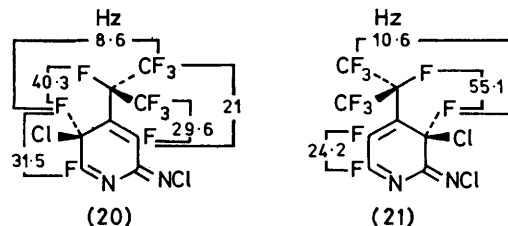
the vinylic fluorine at C-5 can be ascribed to the buttressing effect of the chlorine substituent at C-3, which results in appreciable coupling between only one (*anti* to chlorine) of these groups and the fluorine of CFCl. We conclude that the 1,4-diene is locked in conformation (20), and assign the analogous structure (21) to the 1,3-diene.

EXPERIMENTAL

N.m.r. Data.—Chemical shifts to high field of reference absorptions (external CF_3CO_2H for ^{19}F; external Me_4Si for ^{1}H) are designated negative.

Aminations.—(i) 4-*Methyl*-2,3,5,6-*tetrafluoropyridine* (with Miss B. Melikian). This pyridine (6.5 g, 40 mmol; from [15] C_5F_5N + MeLi) was heated (150 °C for 8 h) with an excess of aqueous ammonia (*d* 0.880; 20 cm³) in the absence of air in a Pyrex ampoule (100 cm³). The yellow solid formed was separated chromatographically (100 × 3 cm Florisil eluted with $CHCl_3$) into 2-amino-3,5,6-trifluoro-4-methylpyridine (4.18 g, 25.8 mmol, 64.5%), m.p. [from light petroleum (b.p. 40—60 °C)] 107 °C (lit.,[15] 106—107 °C) and possessing the correct [19]F n.m.r. parameters,[15b] and 2,6-*diamino*-3,5-*difluoro*-4-*methylpyridine* {0.4 g, 2.5 mmol, 6% [from light petroleum (b.p. 40—60 °C)]} [Found: C, 45.0; H, 4.5; F, 23.4; N, 26.5%; *M* (mass), 159. $C_6H_7F_2N_3$ requires C, 45.3; H, 4.4; F, 23.9; N, 26.4%; *M*, 159], m.p. 149—151 °C (needles) δ_F (saturated solution in $CDCl_3$; 56.5 MHz) −77.1 p.p.m., δ_H (same solution) +2.14 (t, Me) and +3.86br (s, NH_2) p.p.m. (relative intensity 3 : 4).

(ii) *Perfluoro-*(4-*isopropylpyridine*). The literature method [16] was greatly improved, as follows. A mixture of perfluoro-(4-isopropylpyridine) (10.0 g, 31.3 mmol; from [17] C_5F_5N + $CF_3CF:CF_2$–CsF), aqueous ammonia (*d* 0.880; 42 cm³), and tetrahydrofuran (250 cm³) was heated under reflux for 5 h. The product was poured into water (420 cm³) and the resultant mixture was extracted with ether (3 × 330 cm³). Distillation of the dried ($MgSO_4$) extract gave perfluoro-(2-amino-4-isopropylpyridine) (7.0 g, 22 mmol, 71%), b.p. 40—41 °C at *ca.* 1 mmHg, showing only one peak when examined by g.l.c. (2 m SE30; 150 °C) and possessing the correct spectral (i.r., n.m.r.) characteristics.

(iii) 4-*Chloro*-2,3,5,6-*tetrafluoropyridine*. A mixture of 4-chlorotetrafluoropyridine (3.00 g, 16 mmol; from [18] C_5F_5N + $CaCl_2$), tetrahydrofuran (70 cm³), and aqueous ammonia (*d* 0.880, 14 cm³) was heated at 60 °C for 20 h in a

Pyrex ampoule (300 cm³) on a horizontal shaker. The product was poured into water (150 cm³) and then extracted with diethyl ether (3 × 100 cm³); the dry ($MgSO_4$) extract was evaporated and the residue was sublimed at 70 °C (bath) and *ca.* 1 mmHg to yield 2-amino-4-chlorotrifluoropyridine (2.80 g, 15 mmol, 93%) (Found: C, 33.1; H, 0.8; N, 15.0. Calc. for $C_5H_2ClF_3N_2$: C, 32.9; H, 1.1; N, 15.3%), m.p. 115—116 °C (lit.,[19] 117—117.5 °C), $\lambda_{max.}$ (mull) 2.86 and 3.01 μm (N–H stretch), δ_F (84.6 MHz; CCl_4 solution) −15.1 (6-F), −67.3 (3-F), and −82.9 (5-F) p.p.m. (relative intensity 1 : 1 : 1).

(iv) 2,3,5,6-*Tetrafluoropyridine*. This pyridine (2.5 g, 16.5 mmol) (from [20] 4-$H_2NHNC_5F_4N$ + $CuSO_4$) was aminated exactly as described in experiment (iii) above except that a reaction period of 35 h was used. The same work-up procedure provided 2-*amino*-3,5,6-*tetrafluoropyridine* (1.85 g, 12.5 mmol, 76%) (Found: C, 40.5, H, 1.8; F, 38.2; N, 19.2. $C_5H_3F_3N_2$ requires C, 40.5; H, 2.0; F, 38.5; N, 18.9%), m.p. 96—97 °C, $\lambda_{max.}$ (mull) 2.85, 2.99, 3.04sh (N–H stretch), and 3.24 (C–H stretch) μm, δ_F ($CHCl_3$; 84.6 MHz) −15.9 (6-F), −62.5 (3-F), and −74.5 (5-F) p.p.m. (relative intensity 1 : 1 : 1), *m/e* 148 (M^+, 100%).

Chlorinations.—(i) 2-*Amino*-3,5,6-*trifluoro*-4-*methylpyridine*. A solution of the amine (1.6 g, 9.9 mmol) in AnalaR carbon tetrachloride (150 cm³) was added dropwise during 45 min to a cold (−23 °C) stirred solution of t-butyl hypochlorite (2.47 g, 22.8 mmol) in the same solvent (40 cm³). The mixture was stirred at −23 °C for 1.5 h then allowed to warm to room temperature. Removal of carbon tetrachloride at low pressure (20 °C; continuous pumping) left a yellow oil containing a solid; the oil, which had turned red overnight (stored at 0 °C), was decanted from the solid material and distilled to give 3-chloro-6-chloroimino-2,3,5-trifluoro-4-methyl-1-azacyclohexa-1,4-diene (0.7 g, 3.0 mmol, 30%), b.p. 40 °C at *ca.* 1 mmHg, $\lambda_{max.}$ (film) 5.88s and 5.95s μm (CF=N and C=C stretch respectively). During the distillation a solid collected in the water-cooled condenser; this was combined with the solid material mentioned above and the whole sublimed at 80 °C and *ca.* 0.1 mmHg pressure to provide 3-*chloro*-3,5-*difluoro*-6-*chloroimino*-4-*methyl*-2-*oxo*-1-*azacyclohex*-4-*ene* (0.3 g, 1.3 mmol, 13%) (Found: C, 31.6; H, 1.7; Cl, 30.7; N, 12.0. $C_6H_4Cl_2F_2N_2O$ requires C, 31.4; H, 1.7; Cl, 31.0; N, 12.2%), $\lambda_{max.}$ (mull) 3.10, 3.12br (d, N–H stretch), 5.75 (C=O stretch), 5.89 (MeC=CF stretch), and 6.20 (N–H deformation) μm, δ_F (10% solution in $CDCl_3$; 94.1 MHz) −35.2 (d, 3-F; $|J_{35}|$ 10.2 Hz) and −52.6 (dq, 5-F; $|J_{5,Me}|$ 3.4 Hz) p.p.m., δ_H (100 Hz) 2.13 (d, Me) and 8.9 (NH), *m/e* (only [35]Cl-containing species listed; correct isotopic abundances were observed) 228 (M^+, 15%), 193 [(M^+ − Cl·), 83%], 165 [(M^+ − Cl· − CO), 13%], 89 ($C_3H_3F_2^+$, 16%), and 36 (HCl⁺, 100%).

Addition of one drop of water to a small sample (0.3 g, 1.3 mmol) of 3-chloro-6-chloroimino-2,3,5-trifluoro-4-methyl-1-azacyclohexa-1,4-diene gave, after 5 min, 3-chloro-3,5-difluoro-6-chloroimino-4-methyl-2-oxo-1-azacyclohex-4-ene (0.25 g, 1.1 mmol, 85%), spectroscopically (i.r.) identical with the material described above.

(ii) *Perfluoro-*(2-*amino*-4-*isopropylpyridine*). A solution of the amine (4.0 g, 13 mmol) in redistilled carbon tetrachloride (40 cm³) was added dropwise during 20 min to a cold (−16 °C) stirred solution of t-butyl hypochlorite (3.1 g, 29 mmol) in the same solvent (64 cm³) under dry nitrogen. The mixture was stirred at *ca.* −16 °C for 1.5 h then warmed to room temperature. Removal of carbon tetra-

chloride at reduced pressure, followed by distillation of the residue in the apparatus used to purify *NN*-dichloro-pentafluoroaniline,[2] provided *perfluoro*-[2-(*dichloroamino*)-4-*isopropylpyridine*] (4.0 g, 10 mmol, 77%) (Found: C, 25.1; N, 7.2. $C_8Cl_2F_{10}N_2$ requires C, 24.9; N, 7.3%), yellow oil, δ_F (86.4 MHz) $+3.3$ [$(CF_3)_2CF$], -5.1 (6-F), -37.2 (3-F), -49.1 (5-F), and -101.1 [$CF(CF_3)_2$] p.p.m. (relative intensity 6 : 1 : 1 : 1 : 1). This product was stored under nitrogen at -78 °C until required.

(iii) 2-*Amino*-4-*chloro*-3,5,6-*trifluoropyridine*. A solution of the amine (4.0 g, 22 mmol) in AnalaR chloroform (80 cm³) was added dropwise during 30 min to a cold (-16 °C) stirred solution of t-butyl hypochlorite (5.1 g, 47 mmol) in AnalaR carbon tetrachloride (100 cm³) under dry nitrogen. The mixture was stirred at *ca.* -16 °C until chlorination was complete (the progress of the reaction was monitored using i.r. spectroscopy), allowed to warm to room temperature, then evaporated *in vacuo*; distillation of the residue [as in (ii) above] provided 4-*chloro*-2-(*dichloroamino*)-3,5,6-*trifluoropyridine* (4.6 g, 18 mmol, 82%) (Found: C, 23.6; Cl, 42.0; F, 22.2; N, 10.9. $C_5Cl_3F_3N_2$ requires C, 23.85; Cl, 42.3; F, 22.7; N, 11.1%), pungent smelling yellow oil, δ_F (neat; 84.6 MHz) -6.0 (dd, 6-F; $|J_{36}|$ 26.5, $|J_{56}|$ 21.5 Hz), -42.2 (dd, 3-F; $|J_{35}|$ 2.5 Hz), and -53.8 (dd, 5-F) p.p.m.

(iv) 2-*Amino*-3,5,6-*trifluoropyridine*. The previous experiment was repeated, using 2-amino-3,5,6-trifluoro-pyridine (2.0 g, 13.5 mmol) in chloroform (60 cm³) and t-butyl hypochlorite (3.1 g, 28.5 mmol) in carbon tetrachloride (70 cm³), to give (after 45 min at -16 °C) 2-(dichloroamino)-3,5,6-trifluoropyridine (2.8 g, 12.9 mmol, 96%), δ_F (neat; 84.6 MHz) -9.2 (ddd, 6-F; $|J_{36}|$ 29.5, $|J_{56}|$ 22.5, $|J_{6,H}|$ 6.3 Hz), -41.0 (dt, 3-F; $|J_{35}|$ 6.8 Hz), and -52.5 (dt, 5-F; $|J_{3H}| = |J_{5H}| \simeq 6.8$ Hz) p.p.m., δ_H (90 MHz) 7.86.

Reactions of Perfluoro-[2-(*dichloroamino*)-4-*isopropylpyr-idine*].—(i) *Rearrangement*. A small crystal of iodine was added to a stirred solution of perfluoro-[2-(dichloroamino)-4-isopropylpyridine] (2.5 g) in redistilled carbon tetra-chloride under an atmosphere of dry nitrogen. After 1 h, the solvent was removed *in vacuo* and the residue was purified by vacuum distillation (using a nitrogen 'bleed' to eliminate hydrolysis of the distilland by moist air) to provide a 60 : 40 (by ¹⁹F n.m.r.) mixture (1.5 g, 60%) of perfluoro-(3-chloro-6-chloroimino-4-isopropyl-1-azacyclohexa-1,4-diene) and perfluoro-(5-chloro-6-chloro-imino-4-isopropyl-1-azacyclohexa-1,3-diene) (Found: C, 25.6; Cl, 16.2; F, 49.2; N, 6.6. Calc. for $C_8Cl_2F_{10}N_2$: C, 24.9; Cl, 18.4; F, 49.35; N, 7.3%).

(ii) *Thermolysis*. A small Pyrex test tube containing perfluoro-[2-(dichloroamino)-4-isopropylpyridine] (1.2 g, 3.2 mmol) was lowered into a pre-heated oil-bath (165 °C) sited behind a blast screen. Vigorous evolution of a gas capable of bleaching damp litmus paper occurred immediately. After 5 min, the dark, oily product was allowed to cool to room temperature; the solid thus obtained was recrystal-lized from light petroleum (b.p. 60—80 °C) to yield *per-fluoro*-(4,4'-*di*-*isopropyl*-2,2'-*azopyridine*) (0.85 g, 1.35 mmol, 84%) (Found: C, 30.3; F, 60.1; N, 9.1. $C_{16}F_{20}N_4$ requires C, 30.6; F, 60.5; N, 8.9%) as fine orange needles, m.p. 194—196 °C, δ_F (86.4 MHz; Me₂CO) $+2.5$ [$(CF_3)_2CF$], -7.5 (6-F), -46br (3-, 5-F), and -101.5 [$CF(CF_3)_2$] p.p.m. (relative intensity 6 : 1 : 2 : 1), *m/e* 628 ($M^{+\cdot}$, <1%), 609 [$(M^{+\cdot} - F\cdot)$, 16%], 300 ($C_8F_{10}N^+$, 100%), and 69 (CF_3^+, 86%).

Reactions of 4-*Chloro*-2-(*dichloroamino*)-3,5,6-*trifluoropyr-idine*.—(i) *Rearrangement*. A small crystal of iodine was added to a cold (-16 °C) stirred solution of the dichloro-amino-compound (3.0 g) in AnalaR carbon tetrachloride (30 cm³) under dry nitrogen. After 1 h, the mixture was allowed to warm to room temperature then evaporated at reduced pressure; vacuum distillation (using a nitrogen 'bleed') of the oily yellow residue provided a 90 : 10 (by ¹⁹F n.m.r.) mixture (2.6 g, 87%) (Found: C, 24.1; Cl, 42.0; F, 22.9; N, 10.9. Calc. for $C_5Cl_3F_3N_2$: C, 23.9; Cl, 42.3; F, 22.7; N, 11.1%), b.p. 45 °C at *ca.* 0.3 mmHg, of 3,4-dichloro-6-chloroimino-2,3,5-trifluoro-1-azacyclohexa-1,4-diene and 4,5-dichloro-6-chloroimino-2,3,5-trifluoro-1-azacyclohexa-1,3-diene.

With great difficulty, a pure sample of the pale yellow 1,4-*diene*, $\lambda_{max.}$ (film) 5.89s (CF=N stretch) and 6.03s (CF=CCl stretch) μm, was isolated by g.l.c. (2.5 m Celite-OV17; 120 °C) for ¹⁹F n.m.r. analysis; afterwards, a portion (0.3 g, 1.2 mmol) was treated with a trace of water and immediately became converted into 3,4-*dichloro*-6-*chloroimino*-3,5-*difluoro*-2-*oxo*-1-*azacyclohex*-4-*ene* (0.27 g, 1.1 mmol, 92%) (Found: C, 24.4; H, 0.2; N, 11.6. C_5-$HCl_3F_2N_2O$ requires C, 24.0; H, 0.4; N, 11.2%), pale yellow solid, m.p. 101—102 °C, $\lambda_{max.}$ (mull) 3.10br (N⁻H stretch), 5.79 (C=O stretch), 5.98 (CF=CCl stretch), and 6.22 (N⁻H deformation) μm, δ_F (84.6 MHz; Me₂CO) -32.1 (CFCl), and -46.8 (CF=CCl) p.p.m. (relative intensity 1 : 1), *m/e* 248 [$M^{+\cdot}$ (³⁵Cl), 50%], 213 [$M^{+\cdot}$ − Cl· (³⁵Cl), 91%], and 170 ($C_4{}^{35}Cl^2F_2N^+$, 100%) (correct isotopic abundances were observed).

A small sample of the 1,3-diene was also isolated by g.l.c. (2.5 m Celite-OV17, 120 °C), but before it could be examined spectroscopically it changed (on contact with glass) into a very pale yellow solid that was identified as 4,5-dichloro-6-chloroimino-3,5-difluoro-2-oxo-1-azacyclohex-3-ene by n.m.r. spectroscopy, δ_F (84.6 MHz; CCl₄; 50 °C) -23.9 (CFCl) and -42.4 (CF=CCl) p.p.m. (relative intensity 1 : 1), δ_H (CCl₄; external 1,4-$C_6H_4Cl_2$ as reference) -2.0 (br.; NH).

(ii) *Thermolysis*. Using the technique employed with perfluoro-[2-(dichloroamino)-4-isopropylpyridine] (see above), the 4-chloro-analogue (1.0 g, 4 mmol) was converted into *perfluoro*-(4,4'-*dichloro*-2,2'-*azopyridine*) (0.55 g, 1.5 mmol, 75%) (Found: C, 33.2, Cl; 20.0; F, 31.6; N, 15.3. $C_{10}Cl_2F_6N_4$ requires C, 33.2; Cl, 19.7; F, 31.6; N, 15.5%), isolated as orange crystals, m.p. 186—187 °C, *via* recrystal-lization from light petroleum (b.p. 60—80 °C).

Reactions of 2-(*Dichloroamino*)-3,5,6-*trifluoropyridine*.— (i) *Rearrangement*. A small crystal of iodine was added to a solution of the dichloroamino-compound (1.40 g) in AnalaR carbon tetrachloride (50 cm³) under dry nitrogen. The mixture was stirred for 30 min, then evaporated under reduced pressure at 20 °C; vacuum distillation of the residue (using a nitrogen 'bleed') provided a 94 : 6 (by ¹⁹F n.m.r.) pale yellow mixture (1.20 g, 86%) (Found: C, 27.4; H, 0.2; Cl, 32.9; F, 26.0; N, 12.6. Calc. for $C_5HCl_2F_3N_2$: C, 27.7; H, 0.5; Cl, 32.7; F, 26.3; N, 12.9%), b.p. 33 °C at *ca.* 0.5 mmHg, of 3-chloro-6-chloroimino-2,3,5-trifluoro-1-azacyclohexa-1,4-diene and 5-chloro-6-chloroimino-2,3,5-trifluoro-1-azacyclohexa-1,3-diene, $\lambda_{max.}$ (film) 3.23w (C⁻H stretch), 5.88s (CF=N stretch), and 5.96s (CF=CH stretch) μm. An exothermic reaction occurred when water (4 drops) was added to a sample (0.8 g, 3.6 mmol) of the mix-ture of azacyclohexadienes; the solid produced was sub-limed at <1 mmHg pressure (bath temperature 100 °C)

to give pale yellow 3-*chloro*-6-*chloroimino*-3,5-*difluoro*-2-*oxo*-1-*azacyclohex*-4-*ene* (0.65 g, 3.02 mmol, 82%) (Found: C, 28.0; H, 0.9; F, 18.5; N, 13.3. $C_5H_2Cl_2F_2N_2O$ requires C, 27.9; H, 0.9; F, 17.7; N, 13.0%), m.p. 117—118 °C, $\lambda_{max.}$ (mull) 3.10br (N–H stretch), 5.78 (C=O stretch), 5.89 (CH=CF stretch), and 6.21 (N–H deformation) μm, δ_F (CDCl$_3$; 84.6 MHz) -25.6 (dd, 3-F; $|J_{35}|$ 10, $|J_{3,H}|$ 7 Hz), and -46.5 (t, 5-F; $|J_{5H}|$ 10 Hz) p.p.m., δ_H (90 MHz) 6.59 (4-H) and 8.95 (NH).

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