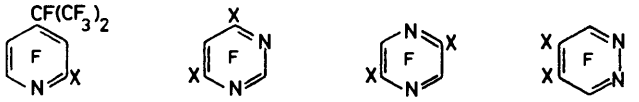
Polyhalogenoaromatic Compounds. Part 34.[1] Syntheses of Perfluoro-aza- and -diaza-cyclohexadiene Derivatives by Fluorination of Perfluoro-azines and -diazines

By **Robert N. Barnes, Richard D. Chambers,* Robert D. Hercliffe,** and **W. Kenneth R. Musgrave,**
Department of Chemistry, University Science Laboratories, South Road, Durham DH1 3LE

Fluorination of perfluoroalkyl-pyridines, -pyrimidines, and -pyrazines, using cobalt trifluoride, gave corresponding aza- and diaza-cyclodienes, in some cases in high yields. Perfluoroalkylpyridazines gave products arising from loss of nitrogen and provide a novel route to some highly crowded perfluorinated olefins. Fluorination with elemental fluorine gave an unusual dimer with perfluoropyrimidine, while perfluoroalkylpyridazines gave products similar to those obtained using cobalt trifluoride.

REACTIONS which involve additions to hydrocarbon aromatic systems have been of interest for a long period of time and, understandably, reactions which involve additions to perfluoroaromatic compounds are of considerable interest. Here we describe further fluorinations of some readily available perfluoroaromatic heterocyclic compounds, *i.e.* (1)—(4), as routes to rel

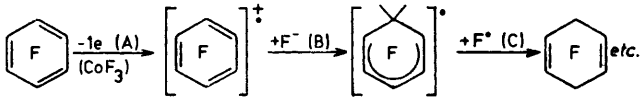


(1) X = F (2) X = C_3F_7 (3) (4) (5) X = C_3F_7

An F in the centre of a ring denotes that all unmarked bonds are to fluorine.

atively inaccessible perfluoro-aza- and diaza-alkenes and dienes. Earlier work has included free-radical chlorination [2,3] and fluorination [4] with cobalt trifluoride, of perfluoro-pyridine, -pyrimidine, and -pyrazine, and direct fluorination of perfluoropyridine has also been reported.[5]

In our earlier work,[4] we concluded that the mechanism of cobalt trifluoride fluorination corresponds to the process outlined in Scheme 1 for hexafluorobenzene, but

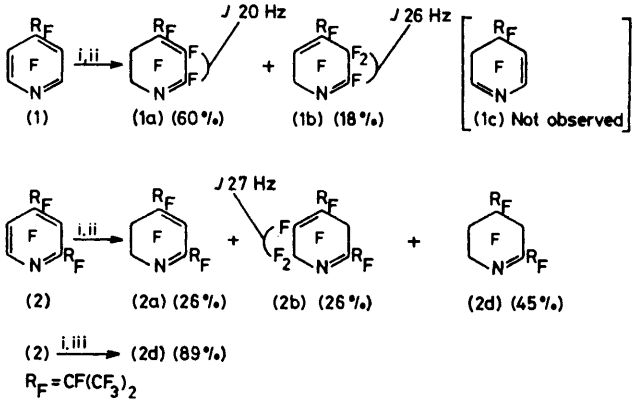


SCHEME 1

also applicable to heterocyclic systems. We reasoned that the replacement of fluorine, attached to an aromatic ring, by a perfluoroalkyl group would make intermediate dienes, *etc.* more easily isolated and this has now been observed.

Fluorinations were carried out using cobalt trifluoride containing calcium fluoride, in order to moderate the reactivity. It is possible that calcium tetrafluorocobaltate is formed in the system, since formation of similar salts, and their use as fluorinating agents, has been demonstrated by Tatlow and his co-workers.[6,7] However, it should be remembered that under the conditions of gradual depletion, used in the fluorination process, there must be a corresponding continuous change in the nature of the fluorinating agent.

Fluorination of the pyridine derivatives (1) and (2) gave good yields of either diene or monoene derivatives, which is in contrast to corresponding fluorinations of pyridine itself [8] or even pentafluoropyridine,[4] where significant ring-opening occurs. At 118 °C a mixture of two dienes (1a) and (1b) was obtained from perfluoro-4-isopropylpyridine (1), with the 1,3-diene predominating. This is in contrast to the product obtained from pentafluoropyridine, where only the corresponding 1,3-diene was observed. Two dienes, (2a) and (2b), were also

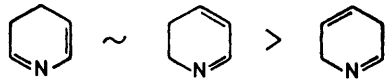


Reagents: i, CoF_3–CaF_2; ii, 118 °C; iii, 170 °C

obtained from perfluoro-2,4-di-isopropylpyridine (2) but, surprisingly, these were accompanied by the monoene derivative (2d) as the major product. At 170 °C an excellent yield of (2d) was obtained but reaction of (1) under these conditions led to a complex mixture containing significant amounts of products arising from ring opening.

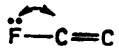
It is interesting to note that no dienes corresponding to the structure (1c) have been obtained in the fluorination of any perfluoropyridine derivatives, even though there seems little reason to believe that there is any inherent great difference in stability between the structures of the skeletons for (1a—c). Indeed, calculations on the order of stability of dihydropyridines indicate the stability

order (6) ~ (7) > (8).[9] Therefore, we attribute the absence of *e.g.* (1c) to the effect of fluorine. It is now well established [10] that an isomer having fluorine attached to



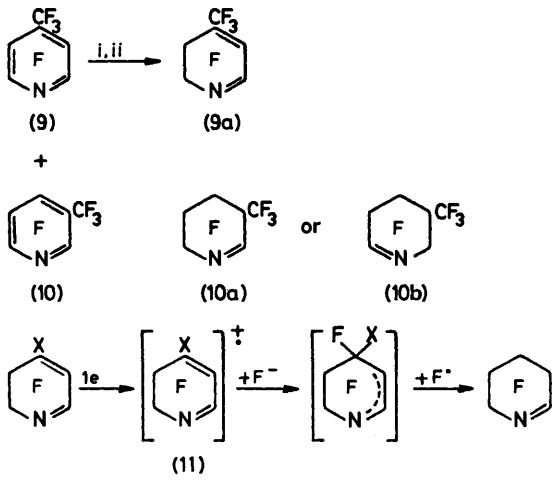
(6) (7) (8)

an olefinic centre is less stable than isomers of the same compound having only perfluoroalkyl groups attached to the centre, due to electron-pair repulsions, involving non-bonding electron pairs on fluorine. Isomer (1c) has three



vinylic fluorine atoms whereas isomers (1a) and (1b) have only two such fluorine atoms and, therefore, would be of lower energy.

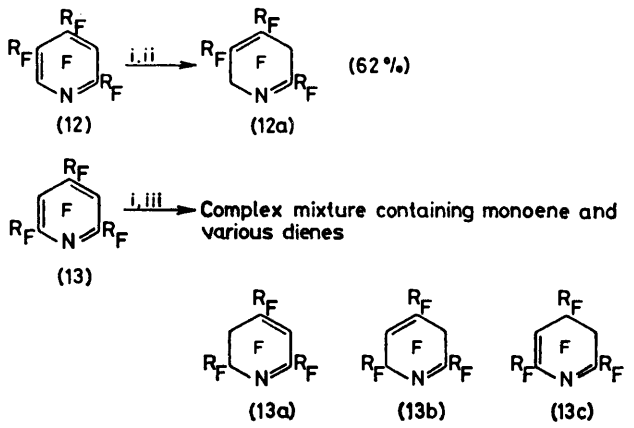
The positional effect of a perfluoroalkyl group on product formation is illustrated by fluorination of a mixture containing (9) and (10); the product contained starting material (55%), together with a diene (9a) (7%) and a monoene thought to have structure (10a) (37%), rather than (10b). Obviously, a trifluoromethyl group



(9) (9a) (10) (10a) (10b) (11)

SCHEME 2 *Reagents*: i, CoF_3, CaF_2; ii, 120 °C

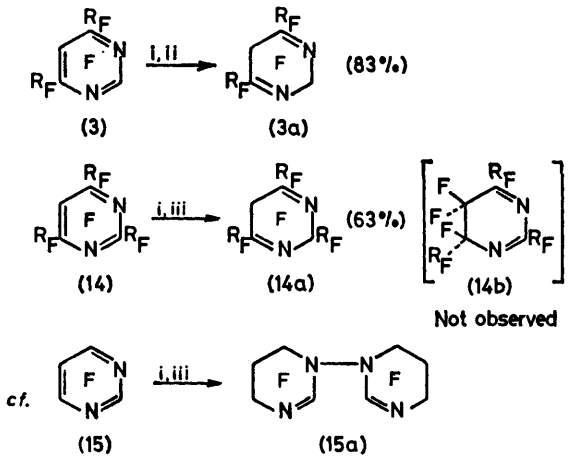
at the 4-position has inhibited reaction and this is consistent with the radical-cation mechanism advanced earlier.[4] It is understandable that transfer of fluoride ion to the intermediate (11) (Scheme 2) would be less efficient with a perfluoroalkyl group at the 4-position since it is established that an olefinic position with fluorine attached is much more susceptible to nucleophilic attack than a corresponding position attached to perfluoroalkyl.[10b] Perfluorotri-isopropylpyridine (12) gave a 1,4-diene (12a), *i.e.* containing no vinylic fluorine atoms, whereas isomer (13) gave a complex mixture which could not be separated. However, g.l.c.–mass spectroscopy indicated a monoene and several dienes. It seems likely that all three dienes (13a—c) are present in this case and the striking contrast in complexity of the pro-



Reagents: i, CoF_3, CaF_2; ii, 138 °C; iii, 145 °C

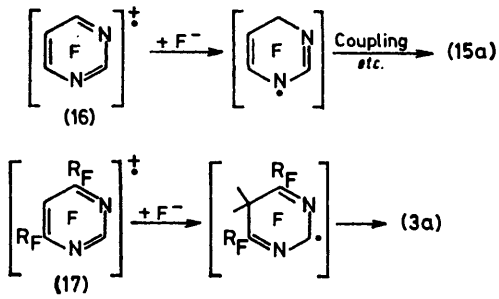
ducts from (12) and (13) is probably attributable to the fact that the dienes (13a—c) each have only one vinylic fluorine atom and therefore have very little difference in stability.

The pyrimidine derivatives (3) and (14) each gave 1,4-diene derivatives, *i.e.* (3a) and (14a) in impressively good

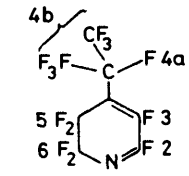


Reagents: i, CoF_3, CaF_2; ii, 172 °C; iii, 183 °C

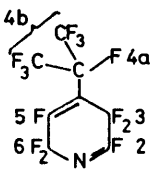
yields for this type of process. Surprisingly, even for the perfluorotri-isopropyl derivative (14), only a 1,4-diene (14a) was observed and it is important to note that neither structures (14a) nor (14b) have fluorine atoms attached to an unsaturated site. This striking select ivity, therefore, reveals another factor which almost



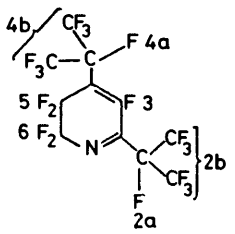
SCHEME 3



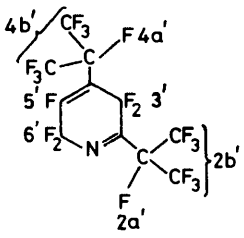
(1a)



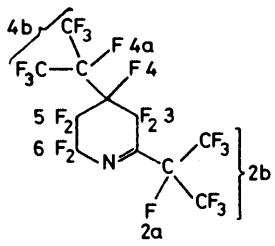
(1b)



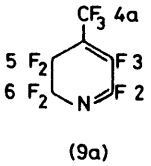
(2a)



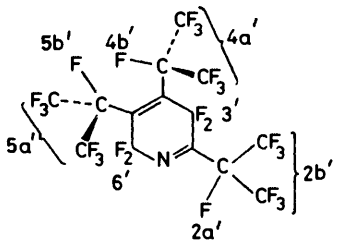
(2b)

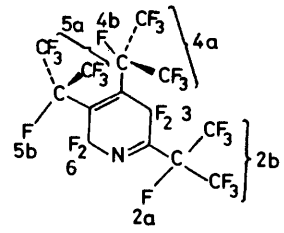


(2d)



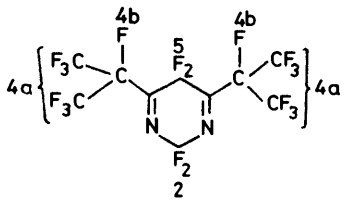
(9a)



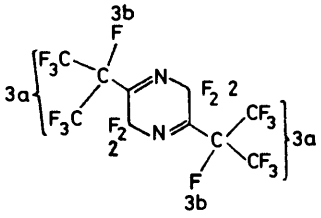


Ratio 2:1 at room temperature

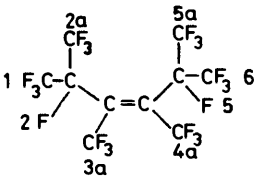
(12a)



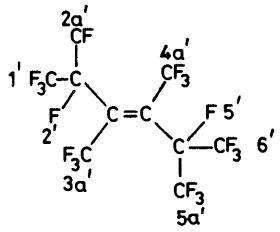
(3a)



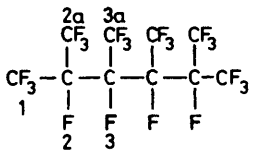
(4a)



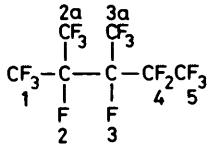
(5a)



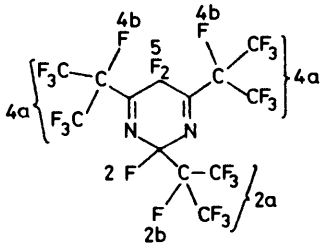
(5b)



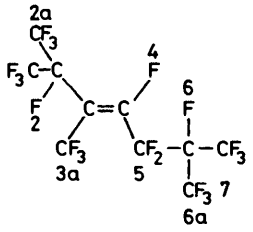
(5c)



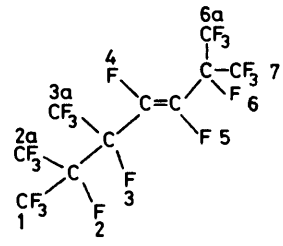
(5d)



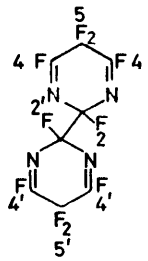
(14a)



(18a)



(18b)

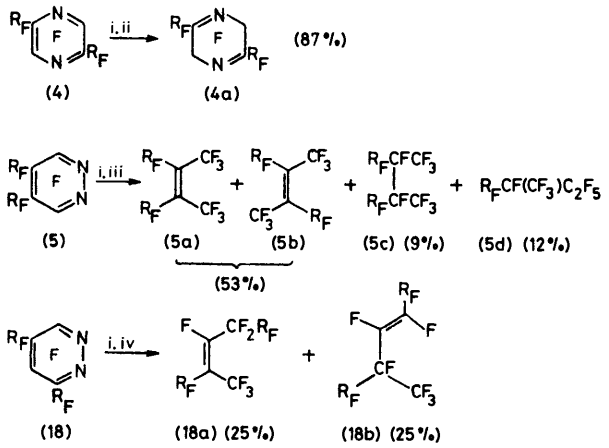


(20)

Numbering systems for n.m.r. assignments

certainly governs the choice between these two isomers Isomer (14b) would have severe eclipsing interactions which are obviously minimised in isomer (14a).

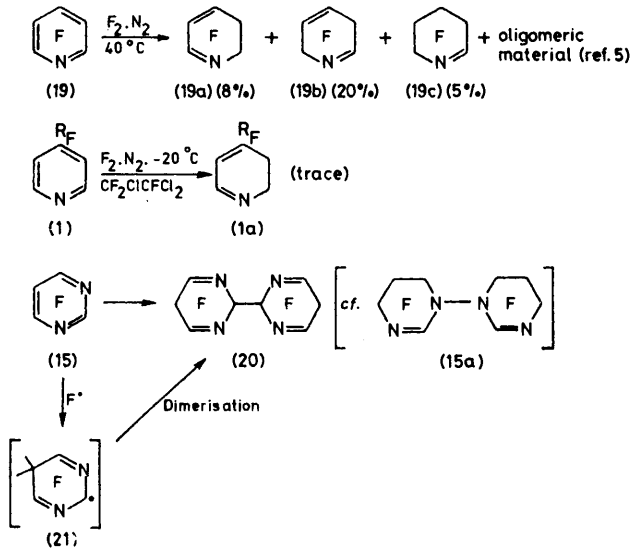
The difference in structure of products formed from (3), (14), and (15),[4] can be accounted for in terms of Scheme 3. Transfer of fluoride ion to the radical-cation intermediate (16) can occur at a position *para* to nitrogen,



SCHEME 4 *Reagents:* i, CoF_3, CaF_2; ii, 156 °C; iii, 163 °C; iv, 132 °C

leading to coupling through nitrogen-stabilised delocalised radicals. However, transfer to radical cation (17) at a position *para* to nitrogen is obviously inhibited by perfluoroalkyl groups and, consequently, transfer *meta* to nitrogen is more likely, as indicated in Scheme 3.

Fluorination of the pyrazine derivative (4) gave an excellent yield of the 1,4-diene (4a) but the pyridazine



SCHEME 5

derivatives (5) and (18) each lost nitrogen on fluorination. However, this provides a novel synthetic approach to some unusual fluorinated alkenes. The products (18a and b) have been represented as the *E*-isomers since only one isomer was identified in each case, as the major products, and steric effects would make these significantly more stable than the corresponding *Z*-isomers.

For comparison, we have carried out a preliminary survey of direct fluorinations of some perfluorinated heterocyclic compounds, which are described in Scheme 5. Tatlow and his co-workers [5] studied direct fluorination of perfluoropyridine (19) and, like these workers, we observed formation of products (19a—c), together with oligomers derived from perfluoropyridine (19), but of uncertain structure. The perfluoro-4-isopropylpyridine (1) was relatively inert, and only a trace of (1a) could be obtained before the conditions led to uncontrolled reaction. More interestingly, perfluoropyrimidine (15) gave a dimeric product (20) and this structure contrasts with that of (15a), which is the product obtained by reaction of (15) with cobalt trifluoride. Compound (20) must be formed by fluorine-atom addition to (15), followed by dimerisation of (21). Addition of the highly electrophilic fluorine atom at a position *meta* to nitrogen in (15) is easily understandable and the different structures of (20) and (15a) provides further strong evidence for the mechanism of cobalt trifluoride fluorinations [4] outlined in Scheme 1.

Derivation of Structures.—Structures of the compounds described, generally followed simply from ^{19}F n.m.r. data as described in the Experimental section, *e.g.* the distinction between the 1,3- (1a) and 1,4- (1b) dienes followed from the coupling of fluorine attached to the unsaturated positions, together with the fact that an isomer of structure (1c), would require an additional 'tertiary' fluorine, at the characteristic high-field position, over structures (1a and b).

EXPERIMENTAL

Spectroscopic data were obtained using the following spectrometers: i.r., Perkin-Elmer 547 or 577; u.v., Pye Unicam S.P. 800; mass, A.E.I. MS9 or V.G. Micromass 12B linked with g.l.c.; n.m.r., Varian A56/60D or Brüker HX90E. Trichlorofluoromethane was used as external standard and upfield shifts (p.p.m.) are recorded as positive. G.l.c. was carried out using a Varian Aerograph instrument fitted with a gas-density balance detector. Two columns were used: Column O, 30% SE 30 on Chromosorb G60—80; and Column A, 20% di-isodecylphthalate on Chromosorb P. A Fischer–Spaltrohr MMS 200 column was used for fractional distillation.

Cobalt Trifluoride Fluorinations.—General procedure. All fluorinations were carried out in a small stirred nickel reactor containing cobalt trifluoride (150 g) and calcium fluoride (150 g). Reactants were dropped from a suitably modified burette directly into the reactor, through which a steady stream of nitrogen was flowing. Products were collected in a liquid-air cooled trap.

(a) *Perfluoro-4-isopropylpyridine* (1). Compound (1) [11] (20.0 g, 62.7 mmol) was fluorinated at 118 °C. The product (22.5 g) was shown (g.l.c.; column A at 80 °C) to consist of a complex mixture of liquids with two major components. Preparative g.l.c. gave *perfluoro-1-aza-4-isopropylcyclohexa-1,3-diene* (1a) (60%) (Found: C, 26.9; F, 68.9; N, 4.2. $C_8F_{13}N$ requires C, 26.9; F, 69.2; N, 3.9%); M^+, 357; $\nu_{max.}$

1 685 and 1 725 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 231 nm (ε 5 060); δ_F 52.5 (d, J 20 Hz, 1 F, 2-F), 76.8 (6 F, 4b-F), 107.2 [d (J 20 Hz) of m, 1 F, 3-F], 102.8 (2 F, 6-F), 114.5 [d (J 35 Hz) of m, 2 F, 5-F], and 185.0 (1 F, 4a-F); and *perfluoro-1-aza-4-isopropylcyclohexa-1,4-diene* (1b) (18%) (Found: C, 26.7; F, 68.9; N, 4.3. $C_8F_{13}N$ requires C, 26.9; F, 69.2; N, 3.9%); M^+, 357; $\nu_{max.}$ 1 720 and 1 765 cm^{-1}; δ_F 57.8 (t, J 26 Hz, 1 F, 2-F), 77.6 (6 F, 4b-F), 88.6 (d, J 26 Hz, 2 F, 6-F), 100.2 (1 F, 5-F), 103.0 (2 F, 3-F), and 188.2 (1 F, 4a-F).

(b) *Perfluoro-2,4-di-isopropylpyridine* (2). (i) Compound (2) [11] (9.5 g, 20.3 mmol) was fluorinated at 118 °C. The product (10.5 g) was not completely separable by g.l.c. (column A at 80 °C and column O at 120 °C) but fractional distillation gave a mixture of perfluoro-1-aza-2,4-di-isopropylcyclohexa-1,3-diene (2a) (26%) and perfluoro-1-aza-2,4-di-isopropylcyclohexa-1,4-diene (2b) (26%), b.p. 142 °C (Found: C, 25.9; F, 70.7; N, 3.1. Calc. for $C_{11}F_{19}N$: C, 26.0; F, 71.2; N, 2.8%); M^+, 507; $\nu_{max.}$ 1 642, 1 688, 1 718, and 1 740 cm^{-1}, δ_F 75.5 (6 F, 2b-, 2b'-, 4b- or 4b'-F), 76.5 (6 F, 2b-, 2b-', 4b-, or 4b'-F), 76.8 (6 F, 2b-, 2b'-, 4b-, or 4b'-F), 77.6 (6 F, 2b-, 2b'-, 4b-, or 4b'-F), 91.1 (d, J 26 Hz, 2 F, 6'-F), 98.4 (2 F, 3'-F), 101.2 (1 F, 3 or 5'-F), 103.0 (1 F, 3 or 5'-F), 110.1 (t, J 7 Hz, 2 F, 6-F), 119.2 (2 F, 5-F), 184.3 (1 F, 2a-, 2a'-, 4a-, or 4a'-F), 186.6 (1 F, 2a-, 2a'-, 4a-, or 4a'-F), 187.9 (1 F, 2a-, 2a'-, 4a-, or 4a'-F), and 191.6 (1 F, 2a-, 2a'-, 4a-, or 4a'-F); and *perfluoro-1-aza-2,4-di-isopropylcyclohex-1-ene* (2d) (45%), b.p. 153 °C (Found: C, 23.9; F, 73.7; N, 2.9. $C_{11}F_{21}N$ requires C, 24.2; F, 73.2; N, 2.6%; M^+, 545); $\nu_{max.}$ 1 711 cm^{-1}; δ_F 72.3 (6 F, 4b-F), 76.1 (6 F, 2b-F), 90.8 and 101.0 (J_{AB} 258 Hz, 2 F, 6-F), 103.5 and 112.8 (J_{AB} 336 Hz, 2 F, 3- or 5-F), 119.6 and 130.2 (J_{AB} 290 Hz, 2 F, 3- or 5-F), 179.6 (1 F, 4- or 4a-F), 183.2 (1 F, 4- or 4a-F), and 191.0 (1 F, 2a-F).

(ii) Compound (2) (17.1 g, 36.5 mmol) was fluorinated at 170 °C. The product (17.5 g) was shown by g.l.c. (Column A at 80 °C) to consist of one major component. Purification by fractional distillation gave perfluoro-1-aza-2,4-di-isopropylcyclohex-1-ene (2d) (89%), identified by comparison of spectroscopic data with that of a sample obtained in (i).

(c) *Perfluoro-3-methylpyridine and perfluoro-4-methylpyridine* (10) *and* (9).[12] A 9 : 1 mixture of compound (10) and compound (9) (8.6 g, 39.3 mmol) was fluorinated at 120 °C. The product (8.8 g) was shown (g.l.c.; column O at 80 °C) to consist of 3 components. Fractional distillation gave perfluoro-1-aza-3-methylcyclohex-1-ene (10a) or perfluoro-1-aza-5-methylcyclohex-1-ene (10b) (45% of the mixture), b.p. 62 °C (Found: C, 24.6; F, 71.2; N, 5.2. Calc. for $C_6F_{11}N$: C, 24.4; F, 70.8; N, 4.8%); M^+, 295; δ_F 41.0 (1 F), 72.2 (3 F), 93.2 and 101.1 (J_{AB} 242 Hz, 2 F), 127.6 and 148.6 (J_{AB} 313 Hz, 2 F), 132.6 and 137.5 (J_{AB} 293 Hz, 2 F), and 177.4 (1 F). A second fraction (b.p. 62—79 °C) was purified by preparative g.l.c. to give *perfluoro-1-aza-4-methylcyclohexa-1,3-diene* (9a) (8% of the mixture) (Found: C, 27.6; F, 66.5; N, 5.6. C_6F_9N requires C, 28.0; F, 66.5; N, 5.5%); M^+, 257; $\nu_{max.}$ 1 761 and 1 765 cm^{-1}; δ_F 52.3 (d, J 18.5 Hz, 1 F, 2-F), 61.9 [d of t, J 22 and 6.5 Hz, 3 F, 4a-F], 103.9 (2 F, 6-F), 114.8 (d of t of q, J 18.5 16, and 22 Hz, 1 F, 3-F), and 117.8 (d of t, J 16 and 6.5 Hz, 2 F, 5-F). The third component (47% of the mixture) was identified as starting material, (10) and (9), (20 : 1) by comparison of spectroscopic data.

(d) *Perfluoro-2,4,5-tri-isopropylpyridine* (12).—Compound (12) [11] (8.1 g, 13.1 mmol) was fluorinated at 138 °C. The product (6.3 g) was shown (g.l.c.; column A at 80 °C) to consist of one major component. Preparative g.l.c. gave *perfluoro-1-aza-2,4,5-tri-isopropylcyclohexa-1,4-diene* (12a) (62%) (Found: F, 73.3. $C_{14}F_{25}N$ requires F, 73.8%); M^+, 657; $\nu_{max.}$ 1 720 and 1 750 cm^{-1}. The n.m.r. spectrum of compound (12a) indicated a mixture of rotational isomers in the ratio 2 : 1. On raising the temperature, signals assigned to 3-, 4-, and 5-Fs showed marked broadening and coalescence. ^{19}F Signals were assigned to the two isomers at room temperature as follows: δ_F 69.7 (2 F, 6- and 6'-F), 70.8 (12 F, 4a-, 5a-, 4a'-, and 5b'-F), 74.7 (6 F, 2b- and 2b'-F), 98.9 (d, J 38 Hz, 3'-F), 99.9 (d, J 38 Hz, 3-F), 159.6 and 164.7 (J_{AB} 176 Hz, 4b'- and 5b'-F), 161.8 (t, J 75 Hz, 5b-F), 170.9 (septet, J 58 Hz, 4b-F), and 190.3 (t, J 38 Hz, 1 F, 2a- and 2a'-F).

(e) *Perfluoro-2,4,6-tri-isopropylpyridine* (13). Compound (13) [11] (7.0 g, 11.3 mmol) was fluorinated at 145 °C. The product (4.8 g) was not completely separable by g.l.c. (columns A and O at various temperatures) and fractional distillation proved unsuccessful. A detailed study by g.l.c.–mass spectroscopy showed two major components, the first of which (M^+, 657) was consistent with any of the dienes (13a—c), but the complexity of the mass spectrum suggested a mixture of all three. The second component (M^+, 695) showed a fairly simple mass spectrum consistent with a monoene.

(f) *Perfluoro-4,6-di-isopropylpyrimidine* (3). Compound (3) [13] (13.4 g, 29.6 mmol) was fluorinated at 172 °C. The product (13.5 g) was shown (g.l.c.; column A at 60 °C) to consist of one major component. Purification by fractional distillation gave *perfluoro-1,3-diaza-4-6-di-isopropylcyclohexa-3,6-diene* (3a) (83%), b.p. 129 °C (Found: C, 24.8; F, 69.2; N, 5.6. $C_{10}F_{18}N_2$ requires C, 24.5; F, 69.8; N, 5.7%); M^+, 490; $\nu_{max.}$ 1 695 and 1 725 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 263 nm (ε 380); δ_F 73.2 (2 F, 2-F), 77.2 (12 F, 4a-F), 113.9 (t, J 30 Hz (2 F, 5-F), and 193.5 (t of septets, J 30 and 6 Hz, 2 F, 4b-F).

(g) *Perfluoro-2,4,6-tri-isopropylpyrimidine* (14). Compound (14) [13] (20.2 g, 33.6 mmol) was fluorinated at 183 °C. The product (18.5 g) was shown (g.l.c.; column A at 90 °C) to consist of a complex mixture of liquids with one major component. Separation by fractional distillation gave *perfluoro-1,3-diaza-2,4,6-tri-isopropylcyclohexa-3,6-diene* (14a) (63%) (Found: F, 70.9. $C_{13}F_{24}N_2$ requires F, 71.2%; M^+, 640; $\nu_{max.}$ 1 690 and 1 724 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 257 nm (ε 500); δ_F 73.7 (6 F, 2a-F), 76.5 (12 F, 4a-F), 110.6 (q, J 32 Hz, 2 F, 5-F), 113.0 (1 F, 2-F), 184.7 (1 F, 2b-F), and 191.7 (t of septets J 32 and 6 Hz, 2 F, 4b-F).

(h) *Perfluoro-2,5-di-isopropylpyrazine* (4). Compound (4) [14] (12.8 g, 28.3 mmol) was fluorinated at 156 °C. The product (11.6 g) was collected as a low-melting white crystalline solid. Recrystallisation from light petroleum (b.p. 60—80 °C) gave *perfluoro-1,4-diaza-2,5-di-isopropylcyclohexa-1,4-diene* (4a) (87%) (Found: C, 24.5; F, 69.3; N, 6.3. $C_{10}F_{18}N_2$ requires C, 24.5; F, 69.8; N, 5.7%); M^+, 490; $\nu_{max.}$ 1 702 and 1 717 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 256 nm (ε 220); δ_F 76.6 (12 F, 3a-F) 88.5 (d, J 29 Hz, 4 F, 2-F), and 191.3 (t of septets, J 29 and 6 Hz, 2 F, 3b-F).

(j) *Perfluoro-4,5-di-isopropylpyridazine* (5). Compound (5) [15] (21.2 g, 46.9 mmol) was fluorinated at 163 °C. The product (17.8 g) was shown (g.l.c.; column A at 60 °C) to be a mixture containing one major and two minor components. Fractional distillation gave *perfluoro-2,3-dimethylpentane* (5d) (12%), b.p. 83 °C (Found: C, 21.9; F, 78.2. C_7F_{16} requires C, 21.6; F, 78.4%; *m/e* 369 (M^+ — F); $\nu_{max.}$ 1 240 cm^{-1}; δ_F 71.9br (9 F, 1-, 2a-, and 3a-F), 82.4 (3 F, 5-F), 115.1 (2 F, 4-F), 177.9 (1 F, 2- or 3-F), and

181.8 (1 F, 2- or 3-F); and perfluoro-2,3,4,5-tetramethylhex-3-ene (5a and b) (53%) ($E + Z$ isomers, 1 : 2.5); b.p. 126 °C (Found: C, 23.8; F, 76.2. Calc. for $C_{10}F_{20}$: C, 24.0; F, 76.0%); *m/e* 481 ($M^+ - F$); $\nu_{max.}$ 1 725 and 1 740 cm^{-1}; δ_F 56.6 (3 a- and 4a-F), 57.6 (3a'- and 4a'-F), 72.3 (12 F, 1-, 2a-, 5a-, 6-, 1'-, 2a'-, 5a'-, and 6'-F), 159.3 (2 and 5-F), and 161.4 (q, J 50 Hz, 2'- and 5'-F). Separation of the pot residue by preparative g.l.c. gave *perfluoro-2,3,4,5-tetramethylhexane* (5c) (9%) (Found: C, 22.4; F, 77.3 $C_{10}F_{22}$ requires C 22.3; F, 77.7%); *m/e* 538 ($M^+ - F$); $\nu_{max.}$ 1 240 cm^{-1}, δ_F 69.0 (6 F, 3a-F), 72.1 (12 F, 1- and 2a-F), 166.6 (2 F, 2- or 3-F), and 170.3 (2 F, 2- or 3-F).

(k) *Perfluoro-3,5-di-isopropylpyridazine* (18). Compound (18) [15] (10.1 g, 22.3 mmol) was fluorinated at 132 °C. The product (8.5 g) was shown (g.l.c.; column O at 25 °C) to consist of three components. Preparative g.l.c. gave (Z)-*perfluoro-2,3,6-trimethylhept-3-ene* (18a) (25%) (Found: F, 76.2. $C_{10}F_{20}$ requires F, 76.0%); M^+, 500; $\nu_{max.}$ 1 671 cm^{-1}; δ_F 62.4 (3 F, 3a-F), 75.8 (6 F, 6a-, and 7-F), 77.3 (d, J 29 Hz, 6 F, 1- and 2a-F), 89.1 (1 F, 4-F), 107.2 (2 F, 5-F), 180.8 (q, J 30 Hz, 1 F, 2-F) and 184.7 (1 F, 6-F); and (Z)-*perfluoro-2,5,6-trimethylhept-3-ene* (18b) (25%) (Found: F, 76.0. $C_{10}F_{20}$ requires F, 76.0%; M^+, 500; $\nu_{max.}$ 1 719 cm^{-1}, δ_F 70.9 (9 F, 1-, 2a-, and 3a-F), 73.9 (6 F, 6a- and 7-F), 126.5 (1 F, 4- or 5-F), 128.7 (1 F, 4- or 5-F), 194.5 (1 F, 2-, 3-, or 6-F), 201.2 (1 F, 2-, 3-, or 6-F), and 207.6 (1 F, 2-, 3-, or 6-F). The third component was identified as starting material (18) by comparison of spectroscopic data with those of an authentic sample.

Direct Fluorinations.—General procedure. All fluorinations were performed by passing fluorine, generated directly and heavily diluted with nitrogen, through a solution of the substrate in 1,1,2-trichlorotrifluoroethane, cooled to the required temperature. The apparatus was designed to eliminate contact of fluorine with anything other than glass, brass, copper, and Fluorolube oil. All usual safety precautions were taken.

(a) *Perfluoro-4-isopropylpyridine* (1). Compound (1) [11] (4.1 g, 12.8 mmol) was dissolved in dry 1,1,2-trichlorotrifluoroethane (7.2 g) and cooled to −20 °C. A mixture of fluorine (1.3 g h^{-1}) and dry nitrogen (40 ml min^{-1}) was bubbled through the vigorously stirred solution for 24 min (*ca.* 1 mol equiv. of fluorine). The product (7.4 g), analysed by g.l.c. (column A at 80 °C) and g.l.c.–mass spectroscopy, contained starting material (1) (64% of the mixture), 1,1,2-trichlorotrifluoroethane (35% of the mixture), and one other component (1% of the mixture), the mass spectrum of which was identical to that of *perfluoro-1-aza-4-isopropylcyclohexa-1,3-diene* (1a).

(b) *Tetrafluoropyrimidine* (15).—Compound (15) [16,17] (5.0 g, 32.9 mmol) was dissolved in dry 1,1,2-trichlorotrifluoroethane (10 g) and cooled to −20 °C. A mixture of fluorine (1.8 g h^{-1}) and dry nitrogen (40 ml min^{-1}) was bubbled through the vigorously stirred solution for 50 min. The product (9.6 g) was shown (g.l.c.; column O at 100 °C) to consist of three major components. Fractional distillation gave 1,1,2-trichlorotrifluoroethane and starting material (22); and vacuum sublimation (40 °C at 0.01 mmHg) of the residual oil gave white crystals of *perfluoro-2,2'-bis-1,3-diazacyclohexa-3,6-dienyl* (20) (22%), m.p. 56—57 °C (Found: C, 27.7; F, 55.9; N, 16.8. $C_8F_{10}N_4$ requires C, 28.0; F, 55.5; N, 16.4%); M^+, 342; δ_F 60.4 (d of d of t, J 24, 24, and 3 Hz, 4 F, 4- and 4'-F), 118.3 (2 F, 2- and 2'-F), 120.9 (t of d, J 24 and 4 Hz, 2 F, 5-F), and 121.2 (t, J 24 Hz, 2 F, 5'-F).

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