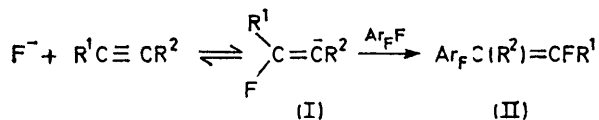


Reactions Involving Fluoride Ion. Part XI.^{1,2†} Syntheses from Hexafluorobut-2-yne

By Richard D. Chambers,* Stafford Partington, and David B. Speight, Department of Chemistry, University Science Laboratories, South Road, Durham

Perfluorobutenide ions, generated by the reaction of fluoride ion with hexafluorobut-2-yne, are trapped by reactive perfluoroaromatic compounds to give perfluorobutenyl derivatives. Further products (a diene and two isomeric trienes) are also obtained from pentafluoropyridine, and cyclisation accompanies reactions with tetrafluoropyridazine, leading to a novel diazaindene. Trifluoro-*s*-triazine gives no useful products and this is attributed to an electron-transfer process.

It is now well established³ that carbanions generated by reaction of fluoride ion with a fluoro-olefin will react with an activated fluoroaromatic system by displacement of fluoride ion. In principle alkenide ions (I) can be generated by an analogous process involving an acetylene activated towards nucleophilic attack, leading to corresponding alkenyl derivatives of fluorinated aromatic compounds (II). This paper describes examples of this

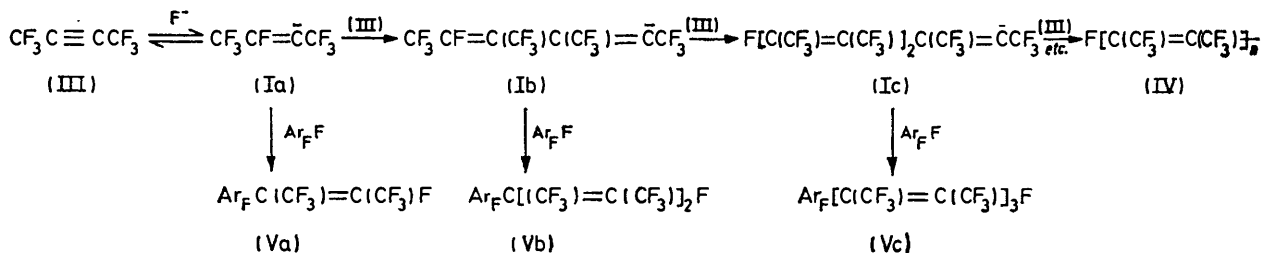


process, involving hexafluorobut-2-yne (I; R¹ = R² = CF₃), which is the most readily available fluorinated acetylene and is known to be susceptible to nucleophilic attack.⁴ However, this acetylene is very readily

present in solution, and (b) by using a very reactive aromatic system.

In our earlier attempts at reaction with pentafluoropyridine, we used sealed reaction vessels and isolated only polymer (IV), with no evidence for incorporation of pentafluoropyridine. We were able, however, to develop a simple atmospheric pressure technique, in which the concentration of acetylene (III) can be maintained at a minimum, and this gave polyfluoroalkenylpyridines (Scheme 2). (*N.B.* This technique was subsequently usefully applied to polyfluoroalkylation reactions.⁷)

Two isomers of perfluoro-4-(1-methylprop-1-enyl)-pyridine were obtained and were easily assigned the *trans*- (VIa) and *cis*- (VIb) structures on the basis of their ¹⁹F n.m.r. spectra, since it has been established⁸⁻¹² that $J(\textit{cis}\text{-CF}_3, \text{CF}_3) > 10$ and $J(\textit{trans}\text{-CF}_3, \text{CF}_3) < 2$ Hz and, likewise, $J(\textit{cis}\text{-CF}_3, \text{F}) \gg J(\textit{trans}\text{-CF}_3, \text{F})$.⁸⁻¹³ Only one



SCHEME 1

polymerised by nucleophiles⁴ and we and others have described the formation of a polymer (IV) with fluoride ion.^{1,2,5,6} If an activated fluoroaromatic compound is present in the system then the extending anion (Ia—c) has a choice between nucleophilic aromatic substitution [to give (Va—c)] or further reaction with the acetylene, which eventually gives the polymer (IV). We have now found that this polymer formation may be limited in two ways: (a) by minimising the concentration of acetylene

† Presented in part at the 7th International Symposium on Fluorine Chemistry, Santa Cruz, U.S.A., July 1973.

¹ Part X, R. D. Chambers, D. T. Clark, D. Kilcast, and S. Partington, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1974, **12**, 1647.

² Preliminary communication, R. D. Chambers, W. K. R. Musgrave, and S. Partington, *Chem. Comm.*, 1970, 1050.

³ See *e.g.* earlier parts of this series or R. D. Chambers, 'Fluorine in Organic Chemistry,' Wiley-Interscience, New York, 1973.

⁴ M. I. Bruce and W. R. Cullen, *Fluorine Chem. Rev.*, 1969, **4**, 79.

⁵ W. T. Flowers, R. N. Haszeldine, and P. G. Marshall, *Chem. Comm.*, 1970, 371.

⁶ J. A. Jackson, *J. Polymer Sci. Part A-1, Polymer Chem.*, 1972, **10**, 2935.

isomer of the diene (VII) was isolated, and the structure is suggested on the basis of the ¹⁹F n.m.r. spectrum (see Experimental section), but two isomers of the triene (VIII) were isolated; nevertheless, it is probable that small amounts of other isomers were present in the mixture in each case. ¹⁹F N.m.r. integrals indicated the structure (VIII) but, so far, we have been unable to make a sufficiently detailed analysis of the spectra to determine the configurations of the side-chain.

The individual methylpropenyl compounds (VIa and b)

⁷ See *e.g.* (a) R. D. Chambers, R. P. Corbally, and W. K. R. Musgrave, *J.C.S. Perkin I*, 1972, 1281; (b) R. D. Chambers and M. Y. Gribble, *ibid.*, 1973, 1405.

⁸ J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, Oxford, 1965, vol. II, p. 912, and references therein.

⁹ D. J. Burton, R. L. Johnson, and R. T. Bogan, *Canad. J. Chem.*, 1966, **44**, 635.

¹⁰ W. T. Miller, R. H. Snider, and R. J. Hummel, *J. Amer. Chem. Soc.*, 1969, **91**, 6532.

¹¹ R. D. Chambers and A. J. Palmer, *Tetrahedron*, 1969, **25**, 4217.

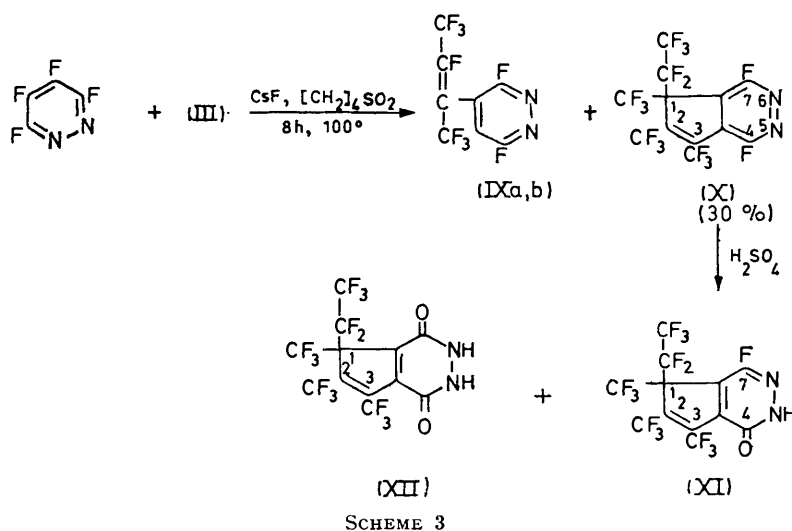
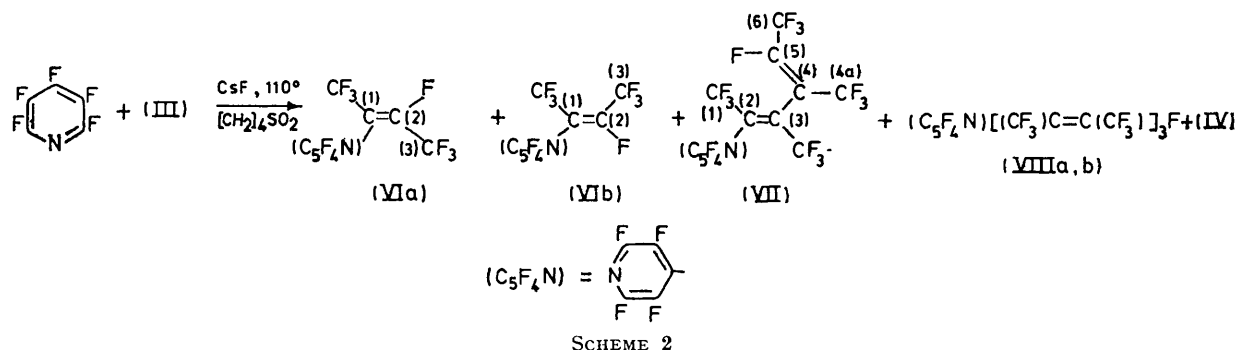
¹² F. E. Herkes and D. J. Burton, *J. Org. Chem.*, 1967, **32**, 1311.

¹³ D. J. Burton and F. E. Herkes, *J. Org. Chem.*, 1968, **33**, 1854.

each give, on further reaction with fluoride ion, the same equilibrium mixture, *i.e.* that containing *ca.* 80% of the *trans*-isomer (VIa). This is consistent with observations^{5,13} of the equilibration of polyfluoro(methylpropenyl)benzenes.^{5,13}

The relative reactivities of the heterocyclic compounds used in this work are indicated by the ratios of the measured rate constants for reaction with ammonia (in

sulphuric acid gave a mixture of amides which could be separated by column chromatography, and one of these (XII) is a diamide, the absence of ring fluorine atoms in which made possible a complete analysis of the ¹⁹F n.m.r. spectrum (see Experimental section). Five separate resonances were observed (intensity ratios 3 : 3 : 3 : 3 : 2), and one of the CF₃ resonances is a singlet, which is consistent with the presence of a CF₃CF₂ group since



aqueous dioxan at 25°)¹⁴ as pentafluoropyridine : tetrafluoropyridazine : tetrafluoropyrimidine : trifluoro-*s*-triazine, 1 : 37 : 1980 : >10⁵, respectively. Consistent with its high reactivity, tetrafluoropyridazine gave reasonable yields of a mixture of *cis*- and *trans*-methylpropenylpyridazines (IXa and b), together with a product which corresponded to the reaction of two molecular proportions of the acetylene (III) with tetrafluoropyridazine. This product, however, has now been shown to be a diazindene (X) and not a diene corresponding to the pyridine derivative (VII).

The ¹⁹F n.m.r. spectrum of (X) at 56.4 MHz was difficult to interpret, but at 100 MHz it was possible to distinguish a low-field resonance attributable to the 4- and 7-fluorine atoms; however long-range coupling involving these ring fluorines made further analysis difficult. Fluorinated pyridazines are very susceptible to acid-induced hydrolysis¹⁵ which involves, specifically, attack at positions *ortho* to nitrogen. The reaction of (X) with

J(CF₃,CF₂) is often small.¹⁶ Of the two possible structures for the corresponding monoamide, the structure (XI) is preferred because the ¹⁹F n.m.r. spectrum reveals coupling involving F(1c) additional to that shown by compound (XII); however the alternative structure cannot be ruled out.

The very reactive tetrafluoropyrimidine gave, at 20°, a high yield of a mixture of *cis*- and *trans*-isomers of perfluoro-4-(1-methylprop-1-enyl)pyrimidine (XIIIa and b); in this case aromatic substitution competes very effectively with oligomerisation of the acetylene (III). A similar reaction at 100° gave (XIIIa and b) together with a small amount of a disubstituted compound (XIV) which has an all-*trans*-configuration of the methylpropenyl groups. Small amounts of components which were

¹⁴ J. S. Waterhouse, Ph.D. Thesis, Durham, 1973.

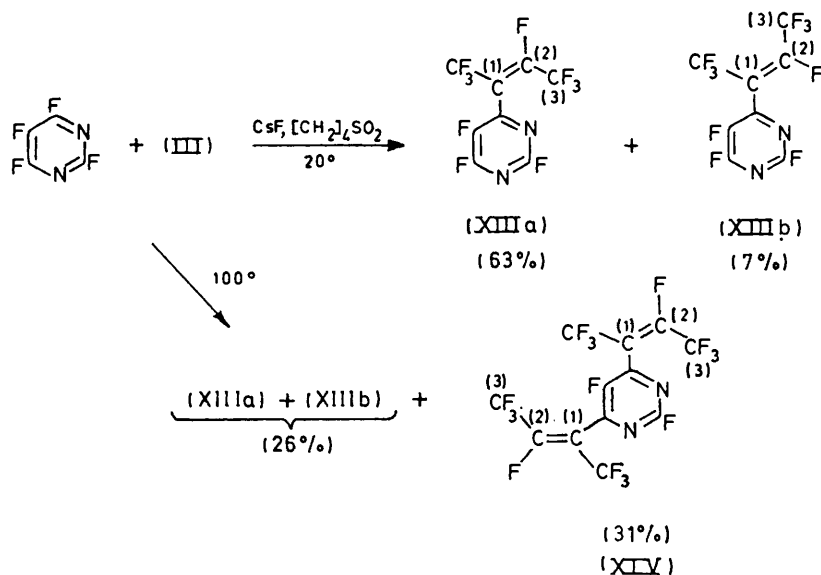
¹⁵ R. D. Chambers, J. A. H. MacBride, and W. K. R. Musgrave, *J. Chem. Soc. (C)*, 1968, 2989.

¹⁶ Ref. 8, p. 877.

not isolated were detected by g.l.c.; these are probably geometric isomers of (XIV).

With the most reactive heterocycle, trimethyl-*s*-triazine, one might anticipate even more efficient trapping of the butenide ion (Ia). Surprisingly, however, no useful products were isolated and substantial amounts of tars were formed. A possible explanation involves a one-electron transfer from the butenide ion (Ia) to the triazine system followed by further reaction of the resultant

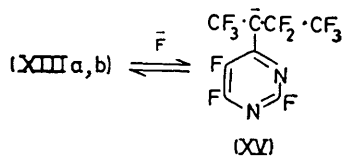
fluoro-(1-methylpropenyl) group or because compounds (XIIIa and b) exist in solution largely as the anion (XV), in the presence of fluoride ion. Unlike the pyridine, however, further reaction of (XIIIa and b) with (III) does take place at 100°, giving (XIV). Similarly, tetrafluoropyridazine has two equivalent reactive sites but these are adjacent and, at 100°, the methylpropenyl derivatives (IXa and b) gave a 44% yield of the diazaindene (X) on further reaction with the acetylene (III).



SCHEME 4

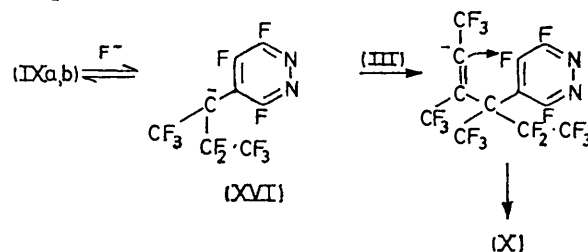
radical anion. We have encountered similar problems in some polyfluoroalkylation reactions involving tetrafluoroethylene,^{7b} and other workers have suggested that electron transfer from $(\text{CF}_3)_3\text{C}^-$ to trityl chloride occurs.¹⁷

Attempts to achieve further reaction of the methylpropenyl compounds (VIa and b), (IXa and b), and (XIIIa and b) with the acetylene (III) revealed a considerable difference in behaviour between the pyridine and the diazine systems. The methylpropenylpyridines (VIa and b) did not react further with (III) at 100° indicating, therefore, that the diene (VII) and triene (VIII) derivatives were formed by reaction of the corresponding anions (Ib and c) with pentafluoropyridine, rather than by successive nucleophilic displacements of vinylic fluorine in (VIa) and (VII) by the butenide anion (Ia). Tetrafluoropyrimidine has two equivalent reactive sites; nevertheless no further reaction of the methylpropenyl derivatives (XIIIa and b) took place at 20°. It



is not clear whether this deactivation of the second site arises simply from the electronic effects of the per-

There are several possible ways in which the diazaindene (X) may be formed: (1) reaction of the dienide ion (Ib) with tetrafluoropyridazine, followed by cyclisation of the product in a process promoted by fluoride ion; (2) formation of perfluoro-4,5-bis-(1-methylprop-1-enyl)pyridazine followed by fluoride-ion promoted cyclisation; (3) reaction of the anion (XVI) with the acetylene (III), followed by cyclisation, or a corresponding concerted process. The last seems probable but, so far, there is insufficient evidence to allow a clear distinction amongst these processes.

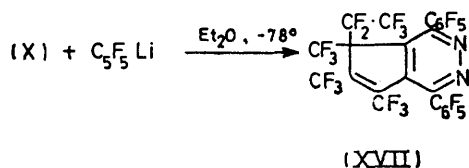


Further proof of the availability of two ring fluorine atoms in (X) was obtained by the reaction with two molecular proportions of pentafluorophenyl-lithium; it is known that tetrafluoropyridazine reacts readily with this lithio-derivative to form tetrakis(pentafluorophenyl)pyridazine.¹⁸

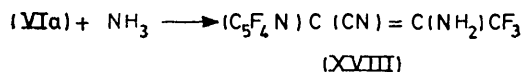
¹⁷ N. I. Delyagina, B. L. Dyatkin, I. L. Knunyants, N. N. Bubnov, and B. Ya. Medvedev, *J.C.S. Chem. Comm.*, 1973, 456.

¹⁸ R. D. Chambers, M. Clark, J. A. H. MacBride, W. K. R. Musgrave, and K. C. Srivastava, *J.C.S. Perkin I*, 1974, 125.

Ammonia reacts with the pyridine derivative (VIa) to give a product similar to that which has been observed



from perfluorobut-2-ene,¹⁹ and the structure (XVIII) is suggested on the basis of the mechanism described for perfluorobut-2-ene.



EXPERIMENTAL

¹⁹F N.m.r. spectra were recorded on a Varian A56/60D spectrometer with CFC₃ as external standard; upfield shifts are quoted as positive.

Reactions with Pentafluoropyridine.—(a) The apparatus used was similar to that described previously,^{7a} the important feature being a circulating pump which enabled gaseous reactant to be passed through a sinter contained in the reaction mixture and then any unchanged gas to be recycled. Caesium fluoride (3 g, 19.7 mmol) and tetramethylene sulphone (100 ml) were introduced into a flask (25 ml capacity) under dry nitrogen. The flask was then evacuated until degassing of the solvent ceased. At this point, hexafluorobut-2-yne (23 g, 142.0 mmol) was introduced from a flexible reservoir (football bladder). The mixture was heated to 110° and pentafluoropyridine (10 g, 59.2 mmol) was introduced, from a syringe, through a serum cap. By using the circulating pump, the perfluorobut-2-yne was bubbled slowly through the mixture. After 2 h at 110°, a partial vacuum had formed and the reaction was quenched by cooling in ice. Volatile material (10.0 g) was then removed by distillation under high vacuum, up to ca. 60°. Analytical scale g.l.c. showed that this volatile material was a multi-component mixture and, by preparative scale g.l.c. it was separated into the following: (i) pentafluoropyridine; (ii) *perfluoro-3,4-dimethyl-2-(4-pyridyl)hexa-2,4-diene* (VII) (2.2 g), b.p. 169° at 760 mmHg (Found: C, 31.6; F, 66.1; N, 2.9%; *M*, 493. C₁₃F₁₇N requires C, 31.6; F, 65.5; N, 2.8%; *M*, 493), λ_{max.} 278 nm (ε 2682). The ¹⁹F n.m.r. spectrum showed sharp, well resolved lines which appeared to arise from a single isomer. Comparison with the spectra of (VIa) and (VIb) (see later) allowed assignments to be made on the basis of chemical shifts; and partial analysis of coupling constants indicates the structure (VII), although this cannot be regarded as completely definitive: ¹⁹F δ (neat liquid) 60.4 (3F, d, *J* 16 Hz, 1-F₃), 62.0br (6F, s, ca. 25 Hz wide, 3- and 4-CF₃), 69.7br (3F, s, ca. 50 Hz wide, 6-F₃), 88.2 (2F, m, pyridine 2- and 6-F), 102.5 [1F, well-resolved m corresponding to overlapping quartets (*J* 16 and 8 Hz) with each of these peaks corresponding to overlapping quartets (*J* ca. 1–2 Hz), 5-F], and 139.5br p.p.m. (2F, m, pyridine 3- and 5-F). The 5-F is therefore coupled with all the CF₃ groups in the side-chain and since the largest coupling is with the 1-F₃, this precludes a *cis*-CF₃C=C(5)F arrangement since *cis*-CF₃F leads to *J* values > 20 Hz.⁸ Likewise, the absence of a clearly defined quartet for the 1-F₃ precludes a *cis*-

C(1)F₃C=C(3)CF₃ arrangement (*J* > 10 Hz); such an arrangement for the 4a- and 6-CF₃ groups is not revealed directly by the spectrum since these resonances are broad, but they could easily contain the required *cis*-CF₃,CF₃ coupling. (iii) The remaining components of the product were isomers of perfluoro-2-(4-pyridyl)-3,4,5,6-tetramethylocta-2,4,6-triene. Isomer (VIIIa) (0.54 g) had b.p. 205° at 760 mmHg (Found: C, 31.4; F, 66.6; N, 1.4%; *M*, 655. C₁₇F₂₃N requires C, 31.1; F, 66.7; N, 2.1%; *M*, 655), λ_{max.} (cyclohexane) 251 and 314 nm (ε 6265 and 3324); ¹⁹F δ (CCl₄) 57.0 (3F), 61.7 (6F), 63.0 (3F), 64.2 (3F), and 70.4 (3F) (CF₃ groups), 88.5br (2F, m, pyridine 2- and 6-F), 100.1br (1F, m, terminal =CF), and 140.5br p.p.m. (2F, pyridine 3- and 5-F); isomer (VIIIb) (1.1 g) had b.p. at 760 mmHg (Found: C, 31.4; F, 67.0; N, 2.2%; *M*, 655%), ¹⁹F δ (CCl₄) 59.7 (9F), 61.5 (3F), 63.0 (3F), and 70.2 (2F) (CF₃ groups), 87.0br (2F, m, pyridine 2- and 6-F), 102.3br (1F, m, terminal =CF), and 138.2 p.p.m. (2F, pyridine 3- and 5-F). We were unable to analyse the n.m.r. spectra of (VIIIa and b) sufficiently well to allow the stereochemistry of the side-chain to be deduced.

(b) *Use of hexafluorobut-2-yne diluted with nitrogen.* A mixture of caesium fluoride (3 g, 19.8 mmol) and tetramethylene sulphone (100 ml) was heated under vacuum and then the system was filled (to 600 mmHg) with dry nitrogen, and pentafluoropyridine (10 g, 59.1 mmol) was introduced. The nitrogen was circulated through the mixture with a pump, and hexafluoro-2-butyne (20 g, 123.4 mmol) was introduced in small amounts (5–10 ml); a partial vacuum was allowed to develop after each addition. After 8 h at 110°, volatile material (12.5 g) was transferred under vacuum and the product mixture obtained was separated by preparative-scale g.l.c., giving: (i) pentafluoropyridine (4.5 g); (ii) *trans-perfluoro-4-(1-methylprop-1-enyl)pyridine* (VIa) (1.5 g, 14%), b.p. 130–131° at 760 mmHg (Found: C, 32.3; F, 62.8; N, 4.5%; *M*, 331. C₉F₁₁N requires C, 32.6; F, 63.2; N, 4.24%; *M*, 331), λ_{max.} (cyclohexane), 278 nm (ε 4180); ¹⁹F δ 61.3 [3F, d of q, *J*(*cis*-CF₃,F) 21 Hz, *J*(CF₃,CF₃) 1 Hz, 1-CF₃], 69.0 [3F, d of q, *J*(*gem*-CF₃,F) 7.5 Hz, *J*(CF₃,CF₃) 1 Hz, 3-F₃], 88.0br (2F, m, pyridine 2- and 6-F), 103.9 [1F, *J*(*cis*-CF₃,F) 21, *J*(*gem*-CF₃,F) 7.5 Hz, 2-F], and 140.0br p.p.m. (2F, m, pyridine 3- and 5-F); and (iii) *cis-perfluoro-4-(1-methylprop-1-enyl)pyridine* (VIb) which was not isolated uncontaminated by the *trans*-isomer (VIa) but showed ¹⁹F δ 57.4 [3F, d of q, *J*(CF₃,CF₃) 11, *J*(*trans*-CF₃,F) 6.5 Hz, 1-CF₃], 67.3 [3F, d of q, *J*(CF₃,CF₃) 11, *J*(*gem*-CF₃,F) 7 Hz, 3-F₃], 88.0br (2F, m, 2- and 6-F), 100.4br (1F, m, 2-F), and 140.0br p.p.m. (2F, m, pyridine, 3- and 5-F).

Reactions with Tetrafluoropyridazine.—A mixture of caesium fluoride (4.0 g, 26.3 mmol) and tetramethylene sulphone (140 ml) was contained in a flask which was evacuated and then filled (to 600 mmHg) with dry nitrogen. Tetrafluoropyridazine (6.3 g, 41.4 mmol) was introduced and the mixture heated to 105°. The nitrogen was circulated through the system and small volumes (ca. 100 mg) of hexafluorobut-2-yne (8.0 g, 49.4 mmol total) were added. After 8 h, volatile material (7.4 g) was transferred under vacuum to a cold trap and analytical scale g.l.c. indicated the presence of a 3–4 component mixture. Careful distillation under vacuum gave a liquid (4.0 g) which was separated by preparative scale g.l.c. into: (i) *cis*- and *trans*-perfluoro-4-(1-methylprop-1-enyl)pyridazine (IX) (0.7 g) (Found: C, 30.3; F, 60.7; N, 9.1%; *M*, 314. Calc. for C₈F₁₀N₂: C, 30.6; F, 60.5; N, 8.9%; *M*, 314), λ_{max.} (cyclohexane) 259 nm (ε 3526); and (ii) tetrafluoropyridazine (2.4 g). The solid

¹⁹ C. G. Krespan, *J. Org. Chem.*, 1969, **34**, 42.

residue was crystallised from dry ether to give *perfluoro-1-ethyl-1,2,3-trimethyl-5,6-diazaindene* (X) (3.6 g, 30%), m.p. 59–60° (Found: C, 29.9; F, 63.5; N, 5.6%; *M*, 476. $C_{12}F_{16}N_2$ requires C, 30.2; F, 63.86; N, 5.9%; *M*, 476), λ_{\max} (cyclohexane) 299 nm (ϵ 5114).

By a procedure similar to that described above, but at 80°, greater yields of (X) (60%) were obtained, together with (IX). At low temperatures (e.g. 0°), and with acetonitrile as solvent, oligomers of hexafluorobut-2-yne were obtained.

The ^{19}F n.m.r. spectrum of (X) showed ^{19}F δ (Me_2CO) 54.9 [3F, $J(2-CF_3, 1-CF_3)$ 10, $J(2-CF_3, 3-CF_3)$ 14 Hz, 2- CF_3], 58.7 [3F, $J(3-CF_3, 4-F)$ 28, $J(3-CF_3, 2-CF_3)$ 14 Hz, 3- CF_3], 60.8 [3F, $J(1-CF_3, 7-F)$ 20, $J(1-CF_3, 1-CF_2)$ 10, $J(1-CF_3, 2-CF_3)$ 10 Hz, 1- CF_3], 78.2 [2F, m, $J(4-F, 3-CF_3)$ 28, $J(7-F, 1-CF_3)$ 20 Hz, 4- and 7-F], 80.0 (3F, s, 1- $CF_2 \cdot CF_3$), and 106.8 p.p.m. [2F, $J(1-CF_2, 1-CF_3)$ 10 Hz, 1- CF_2]. These assignments were made possible by comparison with the spectrum of the hydrolysis product (XII) (see later).

Reactions with Tetrafluoropyrimidine.—(a) At 20°. A flask containing caesium fluoride (3.0 g, 19.7 mmol) and tetramethylene sulphone (25 ml) was evacuated and then the pressure was adjusted to 100 mmHg with dry nitrogen. Tetrafluoropyrimidine (1.5 g, 9.9 mmol) was introduced and then hexafluorobut-2-yne was admitted from a reservoir as the mixture was stirred vigorously. Additions of the acetylene were made until no further uptake was observed [*i.e.* when ca. 1.6 g (9.9 mmol) had been admitted]. Volatile material (2.3 g) was transferred from the mixture under vacuum at ca. 70°. Analytical-scale g.l.c. showed that the volatile material contained tetrafluoropyrimidine and two other components. These were separated by preparative scale g.l.c. and identified as *cis*- and *trans*-perfluoro-4-(1-methylprop-1-enyl)pyrimidine (XIII) (ca. 70% based on 70% conversion) (Found: C, 30.5; F, 60.2; N, 9.1%; *M*, 314. Calc. for $C_9F_{10}N_2$: C, 30.6; F, 60.5; N, 8.9; *M*, 314), *cis*-*trans* ratio 10:90. The *trans*-isomer (XIIIa) showed ^{19}F δ 48.2 (1F, $J_{2,5}$ ca. 26 Hz, pyrimidine 2-F), 62.8 [3-F, d of q, $J(1-CF_3, 2-F)$ 22, $J(CF_3, CF_3)$ 1.5 Hz, 1- CF_3], 72.3 [3F, d of q, $J(CF_3, CF_3)$ 1.5, $J(gem-CF_3, F)$ 7.5 Hz, 3- F_3], 74.0 (1F, $J_{6,5}$ 22 Hz, pyrimidine 6-F), 109.4 [1F, overlapping q of q, $J(2-F, 1-CF_3)$ 22, $J(gem-F, CF_3)$ 7.5 Hz, 2-F], and 154.4br p.p.m. (1F, t, J 25 Hz, pyrimidine 5-F). The *cis*-isomer (XIIIb) showed ^{19}F δ 48.2 (1F, $J_{2,5}$ ca. 26 Hz, pyrimidine 2-F), 59.3 [3F, overlapping d of q, $J(CF_3, CF_3)$ 11, $J(1-CF_3, 2-F)$ 8.5 Hz, 1- CF_3], 70.8 [3F, $J(CF_3, CF_3)$ 12.0, $J(gem-CF_3, F)$ 7.0 Hz, 3- F_3], 74.0 (1F, $J_{6,5}$ 22 Hz, pyrimidine 6-F), 105.6br (1F, 2-F), and 154.4br p.p.m. (1F, t, J ca. 25 Hz, pyrimidine 5-F).

(b) At 100°. An experiment was carried out similar to the one described above but with caesium fluoride (2.5 g, 16.4 mmol), tetramethylene sulphone (25 ml), tetrafluoropyrimidine (1.5 g, 9.9 mmol), and hexafluorobut-2-yne (1.7 g, 10.5 mmol) at 100°. The volatile material (2.3 g) transferred from the mixture was separated by preparative-scale g.l.c. giving (i) *trans*-perfluoro-4,6-bis-(1-methylprop-1-enyl)pyrimidine (XIV) (31% estimated by g.l.c.) (Found: C, 30.2; F, 63.7; N, 5.5%; *M*, 476. $C_{12}F_{16}N_2$ requires C, 30.3; F, 63.9; N, 5.8; *M*, 476). The ^{19}F n.m.r. spectrum indicated a single isomer: δ 49.5br (1F, pyrimidine 2-F), 62.9 [6F, d of q, $J(1-CF_3, 2-F)$ 20, $J(CF_3, CF_3)$ 1.5 Hz, 1- CF_3], 72.4 [6F, d of q, $J(CF_3, CF_3)$ 1.5, $J(1-CF_3, 2-F)$ 7 Hz, 3- F_3], 109.5br (2F, 2-F), and 136.0br p.p.m. (1F, d, J ca. 30 Hz, pyrimidine 5-F), and (ii) *trans*-perfluoro-4-(1-methylprop-1-enyl)pyrimidine (26% estimated by g.l.c.), identified by comparison with an authentic sample (see earlier). The

product also contained a small amount of the corresponding *cis*-isomer, as shown by g.l.c., but this was not isolated.

Reaction of trans-Perfluoro-4-(1-methylprop-1-enyl)pyridine (VIa) with Ammonia.—A solution of (VIa) (0.5 g, 1.51 mmol) in dry ether (ca. 5 ml) was added slowly to ammonia (d 0.880; 4 ml), with stirring, at 0°. After 1 h, a pale yellow solid (0.3 g) was filtered off and recrystallised (methanol) to give *perfluoro-3-amino-2-(4-pyridyl)butyronitrile* (XIX) (0.3 g, 70%), m.p. 138–140° (Found: C, 37.3; F, 47.4; N, 14.3%; *M*, 285. $C_9H_2F_7N_3$ requires C, 37.9; F, 46.7; N, 14.6%; *M*, 285), ^{19}F δ (Me_2CO) 83.4 (3F, =C- CF_3), 95.3 (2F, pyridine 2- and 6-F), and 143 p.p.m. (2F, pyridine 3- and 5-F), λ_{\max} 2.92, 3.0, 3.13 (NH_2), and 4.50 μm (conj. CN).

Reaction of Perfluoro-4-(1-methylprop-1-enyl)pyridazine (IX) with Hexafluorobut-2-yne.—Tetramethylene sulphone (5 ml) and caesium fluoride (0.5 g, 3.3 mmol) were introduced into a flask (10 ml) under dry nitrogen and the flask was evacuated until degassing ceased. Hexafluorobut-2-yne (1.0 g, 6.2 mmol) was allowed into the system until atmospheric pressure was reached and then the methylpropenyl derivative (IX) (0.3 g, 0.96 mmol) was added, giving an immediate intense yellow colour. After 6 h, volatile material was transferred to a cold trap and, after recrystallisation (toluene), gave spectra identical with those from an authentic sample of (X) (0.2 g, 44%).

Reactions of Perfluoro-1-ethyl-1,2,3-trimethyl-5,6-diazaindene (X).—(a) *Hydrolysis.* Compound (X) (1.5 g, 3.15 mmol) was dissolved in concentrated sulphuric acid (10 ml), to which a few drops of water had been added. The solution was heated to 150° for 48 h, cooled, and added dropwise to water (50 ml), with cooling. The resultant precipitate (1.3 g) was filtered off, washed, and crystallised several times from aqueous methanol. Analytical scale g.l.c. showed the presence of a two-component mixture.

This mixture (ca. was dissolved in chloroform (5 ml), to which a few drops of methanol had been added, and the solution was chromatographed on a silica column. Two main fractions were collected which yielded: (i) a white solid, *perfluoro-1-ethyl-1,5-dihydro-1,2,3-trimethyl-5,6-diazainden-4-one* (XI), m.p. 163–165° (0.2 g) (Found: C, 29.9; F, 60.2; N, 6.0%; *M*, 474. $C_{12}HF_{15}N_2O$ requires C, 30.4; F, 60.1; N, 5.9%; *M*, 474), λ_{\max} (cyclohexane) 378 nm (ϵ 4000), ^{19}F δ (Me_2CO) 55.9 [3F, $J(2-CF_3, 3-CF_3)$ 14, $J(2-CF_3, 1-CF_3)$ 11 Hz, 2- CF_3], 60.1 [3F, $J(1-CF_3, 2-CF_3)$ 11, $J(1-CF_3, 7-F)$ 22, $J(1-CF_3, 1-CF_2)$ 11 Hz, 1- CF_3], 61.5 [3F, $J(3-CF_3, 2-CF_3)$ 14 Hz, 3- CF_3], 82.0 (3F, s, 1- $CF_2 \cdot CF_3$), 94.3br (1F, unresolved m, 7-F), and 100.8 p.p.m. [2F, m containing $J(1-CF_2, 1-CF_3)$ 11 Hz, 1- CF_2]; (ii) a pale yellow solid, *perfluoro-1-ethyl-5,6-dihydro-1,2,3-trimethyl-5,6-diazaindene-4,7-dione* (XII), m.p. 207–209° (0.3 g) (Found: C, 30.7; F, 56.6; N, 6.1%; *M*, 472. $C_{12}H_2F_{14}N_2O_2$ requires C, 30.5; F, 56.4; N, 5.93%; *M*, 472), λ_{\max} (cyclohexane) 420 nm (ϵ 9970), ^{19}F δ (Me_2CO) 56.7 [3F, $J(2-CF_3, 3-CF_3)$ 13.5, $J(2-CF_3, 1-CF_3)$ 10 Hz, 2- CF_3], 57.2 [3F, $J(1-CF_3, 1-CF_2)$ 10, $J(1-CF_3, 2-CF_3)$ 10 Hz, 1- CF_3], 59.6 [3F, $J(2-CF_3, 3-CF_3)$ 13.5 Hz, 3- CF_3], 80.5 (3F, s, 1- $CF_2 \cdot CF_3$), and 104.3 p.p.m. [2F, m containing $J(1-CF_2, 1-CF_3)$ 10 Hz, 1- CF_2].

(b) *Reaction with pentafluorophenyl-lithium.* Butyl-lithium (8.8 ml; 2.5M-solution) in dry ether (10 ml) was added, dropwise, to a solution of bromopentafluorobenzene (4.9 g, 19.8 mmol) in dry ether (50 ml) over 30 min at -78° . The mixture was stirred at this temperature and, after 1 h, a solution of (X) (4.7 g, 9.9 mmol) in dry ether (30 ml) was added over 5 min; the addition was associated with the

immediate formation of a brown colour. After 2 h, the mixture was allowed to warm to room temperature and, after stirring for a further 2 h, dilute hydrochloric acid (100 ml) was added. The ether layer was separated, washed, dried (MgSO_4), and evaporated to leave a pale yellow viscous oil (3 g), which readily crystallised from petroleum (b.p. $40-60^\circ$) to give, as a pale yellow solid (2 g), *perfluoro-1-ethyl-1,2,3-trimethyl-4,7-diphenyl-5,6-diazaindene* (XVII), m.p. $162-165^\circ$ (2 g, 26%) (Found: C, 36.9; F, 57.7; N,

4.3%; *M*, 772. $\text{C}_{24}\text{F}_{24}\text{N}_2$ requires C, 37.3; F, 59.0; N, 3.63%; *M*, 772).

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