Polyfluoroheterocyclic Compounds. Part XXV.[1] Thermal Reactions of Perfluoroalkylpyridazines

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Flow pyrolysis of perfluoro-4,5-diethylpyridazine gave mainly perfluoro-4,5-diethylpyrimidine and some perfluoro-2,6-diethylpyrazine; perfluoro-4-ethylpyridazine gave a mixture of perfluoro-4- and -5-ethylpyrimidines; and perfluoro-4-isopropylpyridazine gave a mixture of perfluoro-isopropyl- and -ethyl-pyrimidines. Pyrolysis of perfluoro-4,5-di-isopropylpyridazine has been re-examined under flow and static conditions and a correction to previous conclusions is made. These reactions are explained in terms of formation and rearrangement of diazabenzvalenes. Perfluoro-4,5-diethyl-3,6-di-isopropylpyridazine has been synthesised; pyrolysis led to products arising from both nitrogen elimination and rearrangement. Vacuum pyrolysis of perfluoro-4,5-di-isopropylpyridazine gave significant amounts of fragmentation products.

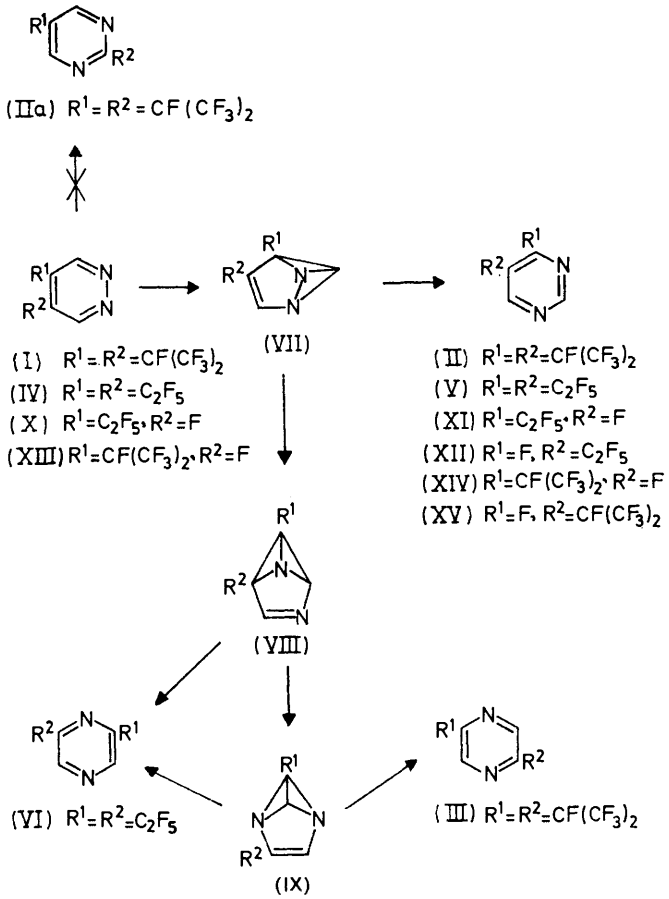
We have described previously [2] a novel thermal rearrangement of perfluoro-4,5-di-isopropylpyridazine (I) to give both a pyrimidine (II) and a pyrazine (III). Also, we have reported reactions of perfluorotetraphenylpyridazine and perfluorodialkyldiarylpyridazines where the dominant process on pyrolysis is elimination of nitrogen.[1] We now report the results of reactions of perfluoro-mono-, di-, and tetra-alkylpyridazines which contrast with our earlier results and also enable us to correct some of our earlier conclusions.[2]

Perfluoro-4,5-diethylpyridazine (IV), which has been prepared previously by polyfluoroalkylation of tetrafluoropyridazine with tetrafluoroethylene [3] or chlorotrifluoroethylene,[4] was pyrolysed at 650° in a stream of dry nitrogen (contact time *ca.* 60 s). The product contained as major component perfluoro-4,5-diethylpyrimidine (V) and a small amount of perfluoro-2,6-diethylpyrazine (VI). The structure of the pyrimidine (V) was easily deduced from its ^{19}F n.m.r. spectrum, which contained a low-field resonance characteristic of F-2 in a pyrimidine system;[2,5] in addition, no high-field resonance, characteristic of F-5, was observed. The pyrazine (VI) was not identical with perfluoro-2,5-diethylpyrazine, prepared [6] by photolysis [7] of the pyridazine (IV), and the perfluoro-2,3-diethylpyrazine structure could be ruled out on the basis of ^{19}F n.m.r. chemical shifts because it is now well established that the downfield shift effect of a perfluoroalkyl group on an *ortho*-fluorine atom is significantly larger than the effect on a *meta*-position.[8] The chemical shift of the low-field peak observed for the ring fluorine atom (65·4 p.p.m.

[1] R. D. Chambers, M. Clark, J. A. H. MacBride, W. K. R. Musgrave, and K. C. Srivastava, *J.C.S. Perkin I*, 1974, 125.
[2] R. D. Chambers, J. A. H. MacBride, and W. K. R. Musgrave, *J. Chem. Soc.* (*C*), 1971, 3384.
[3] R. D. Chambers and M. Y. Gribble, *J.C.S. Perkin I*, 1973, 1406.
[4] R. D. Chambers and M. Y. Gribble, *J.C.S. Perkin I*, 1973, 1411.
[5] R. E. Banks, D. S. Field, and R. N. Haszeldine, *J. Chem. Soc.* (*C*), 1970, 1280.
[6] J. R. Maslakiewicz, unpublished results.
[7] R. D. Chambers, W. K. R. Musgrave, and K. C. Srivastava, *Chem. Comm.*, 1971, 264.
[8] R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, L. H. Sutcliffe, and G. J. T. Tiddy, *Tetrahedron*, 1970, **26**, 71.

upfield from $CFCl_3$, a shift of *ca.* −29 p.p.m. with respect to tetrafluoropyrazine [9]) is only consistent with perfluoro-2,6-diethylpyrazine, in which the substituents are *ortho* and *para* to the ring fluorine atoms.

In earlier discussion [2] we accounted for the rearrangement of (I) to a pyrimidine and a smaller amount of the pyrazine (III) on the basis of the intermediacy of diazabenzvalenes. The structure of the pyrazine (III) has been confirmed, but the work described here shows that the structure (IIa), originally assigned to the pyrimidine obtained from the pyridazine (I), is in error and, indeed, this pyrimidine has structure (II).



SCHEME 1 All unmarked positions carry fluorine

This correction brings with it the advantage of allowing us to account for the observed pyrimidines (II) and (V) and pyrazines (III) and (VI) in one reaction scheme (Scheme 1), rather than the more complicated sequences suggested previously.[2,10] Thus, the 1,2-shift in the relative positions of nitrogen atoms in (I) and (IV) can be accounted for by formation of the intermediate diazabenzvalene (VII), followed by re-aromatisation giving the pyrimidines (II) and (V), respectively. The formation of a pyrazine (VI), in which the relative positions of the perfluoroalkyl groups have also changed by a net 1,2-shift, requires further rearrangement of the diazabenzvalene (VII) to (VIII), followed by rearomatisation to (VI). However, the pyrazine (III) obtained from perfluoro-4,5-di-isopropylpyridazine (I) shows a net 1,3-shift in the relative positions of the perfluoroisopropyl groups, which can be accounted for by the sequence (VII) ⟶ (VIII) ⟶ (IX) ⟶ (III). The diazabenzvalene (IX) could also rearomatise to a pyrazine analogous to (VI); while (III) is the only perfluorodi-isopropylpyrazine which has been isolated, the product also contained amounts of other components which were too small for isolation. This difference, between the pyrazines (III) and (VI), could arise from a greater driving force to separate perfluoroisopropyl than the smaller perfluoroethyl groups in the sequence (VIII) ⟶ (IX).

Under flow conditions, in a stream of nitrogen at atmospheric pressure, isomerisation of (IV) occurs at a temperature (*ca.* 650°) considerably lower than for tetrafluoropyridazine (*ca.* 815°), although well above that required for isomerisation of the perfluorodi-isopropyl derivative (I) (*ca.* 550°). Also, we have now established that rearrangement of (I) occurs at temperatures as low as 300° on prolonged heating in a sealed nickel tube and, at these lower temperatures, there was no evidence of fragmentation and the pyrimidine (II) was the sole product.

According to Scheme 1, a perfluoro-4-alkylpyridazine should lead to a diazabenzvalene (VII), where the perfluoroalkyl group could be at either of the positions occupied by R^1 and R^2. Consequently, rearomatisation would lead to a mixture of perfluoro-4- and -5-alkylpyrimidines. The pyridazine (X) gave a mixture of perfluoroethylpyrimidines (XI) and (XII), and the pyridazine (XIII) gave a mixture of perfluoroisopropylpyrimidines (XIV) and (XV), together with compounds arising from fragmentation of the side chain (see Experimental section). However, we have not been able to detect any pyrazines in the products from reactions of (X) and (XIII).

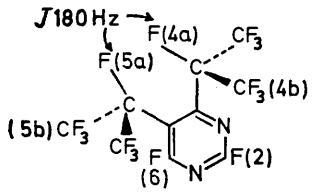
The pyrimidine (II) was originally assigned the structure (IIa) [2] on the basis of calculated ^{19}F chemical shifts, obtained by using substituent chemical shifts (S.C.S.) for $CF(CF_3)_2$ derived from the pyridine system. Now that n.m.r. data are available for the perfluoroisopropylpyrimidines (XIV) and (XV), as well as for other derivatives obtained by direct polyfluoroalkylation of tetrafluoropyrimidine,[11] it is clear that it is invalid to extrapolate the S.C.S. data from the pyridine to the pyrimidine system. Indeed, the structure of (II) cannot be convincingly established on the basis of chemical shifts. However, we have now been able to observe weak side-bands of the tertiary-fluorine resonance which can only arise from coupling between tertiary fluorine atoms in *adjacent* $CF(CF_3)_2$ groups. The spectrum was temperature-invariant and it seems likely that the perfluoroisopropyl groups are in an

[9] R. D. Chambers, J. A. H. MacBride, and W. K. R. Musgrave, *Chem. and Ind.*, 1966, 1721.

[10] R. D. Chambers, M. Clark, J. R. Maslakiewicz, and W. K. R. Musgrave, *Tetrahedron Letters*, 1973, 2405.

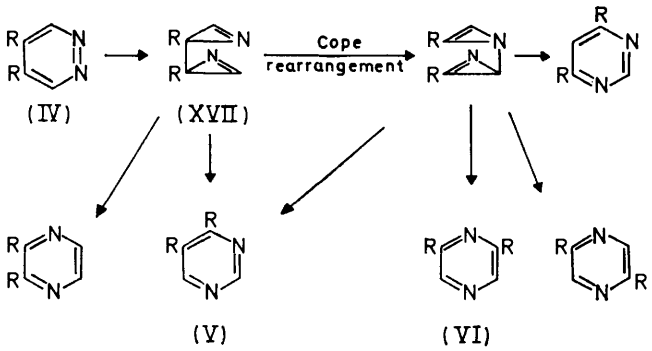
[11] C. J. Drayton, W. T. Flowers, and R. N. Haszeldine, *J. Chem. Soc.* (*C*), 1971, 2750.

effectively fixed conformation, as in (XVI), and the magnitude of J value is a further example of ' through-space ' F–F coupling. [12]



(XVI)

We have recently pointed out that an alternative mechanism for these rearrangements is possible,[10] based on the formation of diazabicyclopropenyls; this is related to rearrangements of tetraphenylbicyclopropenyls to tetraphenylbenzenes,[13] and the rearrangements of furans,[14,15] thiophens,[16] and isoxazoles [17] *via* the formation of cyclopropenyl and azacyclopropenyl rings. The alternative mechanism is illustrated with reference to perfluoro-4,5-diethylpyridazines (IV) in Schemes 1 and 2. In order to produce a pyrimidine and then a pyrazine in which the substituents are separated, a Cope rearrangement of (XVII) must be invoked. However, Scheme 2 shows that there is no apparent reason for the observed specificity leading to (V) and (VI), which is in sharp contrast to the diazabenzvalene mechanism already

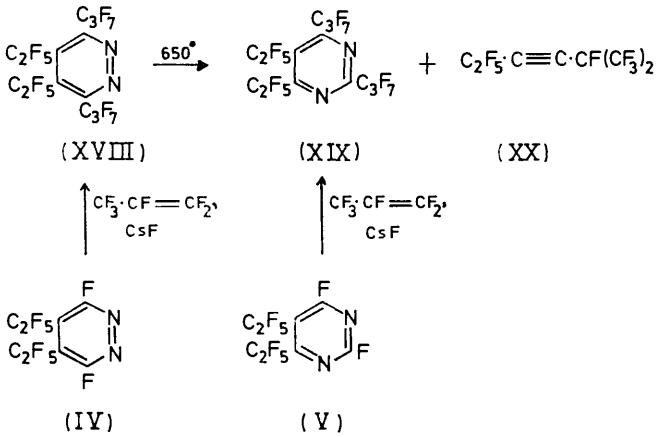


SCHEME 2 R = C_2F_5; all unmarked positions carry fluorine

discussed. Therefore only the latter mechanism accounts for the highly specific substituent labelling as well as the dominance of the pyrimidines over pyrazines in the products.

In discussing the mechanism for these reactions, we have assumed unimolecular processes. This could be confirmed by pyrolyses under vacuum, but direct comparison of reactions under conditions of atmospheric flow and vacuum transfer is complicated by the higher temperature required for the latter, because of the shorter contact times. At these higher temperatures, fragmentation products constitute a significant proportion of the mixture, but, nevertheless, pyrimidines and pyrazines are still observed. We have therefore discounted any bimolecular processes.

Perfluoro-4,5-diethyl-3,6-di-isopropylpyridazine (XVIII), synthesised from perfluoro-4,5-diethylpyridazine by reaction with hexafluoropropene and caesium fluoride, was pyrolysed under vacuum at 650° and gave a mixture containing approximately equal amounts of perfluoro-5,6-diethyl-2,4-di-isopropylpyrimidine (XIX) and perfluoro-5-methylhex-3-yne (X). The pyrimidine (XIX) was identical with the product obtained from perfluoro-4,5-diethylpyrimidine, hexafluoropropene, and caesium fluoride.



Thus we have now observed a whole spectrum of possibilities during pyrolysis: from preferential elimination of nitrogen from pyridazines, *e.g.* in the case of perfluorotetra-aryl derivatives,[1] to rearrangement [2] to pyrimidines and pyrazines in the reactions of (I) and (IV); the production of both pyrimidine (XIX) and acetylene (XX) from the pyridazine (XVIII) demonstrates an intermediate situation. In view of our earlier conclusion that diradical intermediates are produced in these nitrogen extrusion reactions from pyridazines,[1] the major factor governing competition between nitrogen extrusion and rearrangement is probably the ability of the substituents adjacent to nitrogen in the pyridazine to stabilise radicals, *i.e.* aryl > Cl > polyfluoroalkyl > F.

We noted previously [2] that the product mixture from flow pyrolysis of perfluoro-4,5-di-isopropylpyridazine (I) contained fragmentation products which we did not discuss. Pyrolysis under vacuum at 750° gave the same compounds but as a significant proportion of the product together with the pyrimidine (II) and the pyrazine (IV). Elemental analysis of these compounds did not give consistent results but mass spectroscopic data indicate that they are formed by loss of CF_4 and C_2F_6 from the pyridazine (I). Compounds (XXI) and (XXII) were isolated by g.l.c and structures were assigned on the basis of their ^{19}F n.m.r. spectra. Another component,

[12] See R. D. Chambers, L. H. Sutcliffe, and G. J. T. Tiddy, *Trans. Faraday Soc.*, 1970, **66**, 1025, and references therein.

[13] R. Breslow, P. Gal, H. W. Chang, and L. J. Altman, *J. Amer. Chem. Soc.*, 1965, **87**, 5140; V. R. Weiss and S. Andrae, *Angew. Chem. Internat. Edn.*, 1973, **12**, 150, 152.

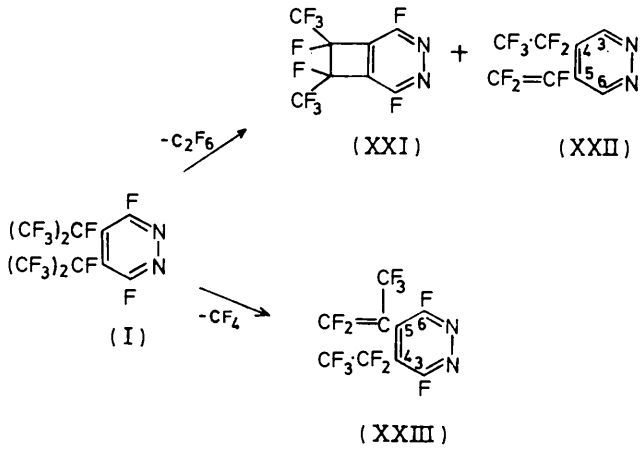
[14] E. E. van Tamelen and T. H. Whitesides, *J. Amer. Chem. Soc.*, 1968, **90**, 3894.

[15] A. Couture and A. Lablache-Combier, *Chem. Comm.*, 1971, 891.

[16] A. Couture and A. Lablache-Combier, *Tetrahedron*, 1971, **27**, 1059.

[17] B. Singh and E. F. Ullmann, *J. Amer. Chem. Soc.*, 1966, **88**, 1844.

possibly having structure (XXIII), was obtained by g.l.c. as a mixture with an isomer of compound (XXI).



EXPERIMENTAL

I.r. spectra were recorded on a Grubb–Parsons Spectromaster, and u.v. spectra on a Unicam SP 800 spectrophotometer. ^{19}F N.m.r. spectra were recorded on a Varian A56/60D spectrometer with $CFCl_3$ as internal reference (upfield shifts are quoted as positive). With reference to chemical shifts and coupling constants for the aromatic diazines, ' a ' denotes fluorine atoms attached to C-1 of the alkyl or alkenyl group, ' b ' those attached to C-2, *etc.* Unless otherwise stated, g.l.c. was performed using silicone elastomer, as stationary phase, on Celite. Tetramethylene sulphone was redistilled *in vacuo* and dried over molecular sieves.

Pyrolysis of Perfluoro-4,5-diethylpyridazine.—Perfluoro-4,5-diethylpyridazine [3,4] (3·5 g) was passed as a vapour in a stream of dry N_2 through a platinum-lined silica tube loosely packed with platinum foil at 650° (contact time *ca.* 60 s). The gas chromatogram of the pyrolysate (3·12 g) showed [apart from small amounts of two products of low retention volume (v_R)] four components in the following proportions in order of elution: A (5), B (85), C (<2), and D (8). Component C, which overlapped with D, the starting pyridazine (from v_R), was formed in insufficient quantity for characterisation. Preparative scale g.l.c. (di-isodecyl phthalate on Celite) furnished pure samples of component A, a liquid identified as *perfluoro-2,6-diethylpyrazine* (Found: C, 27·05; N, 8·35. $C_8F_{12}N_2$ requires C, 27·3; N, 7·95%), ^{19}F δ 65·4 (F-3), 84·25 (CF_3), and 116·5 p.p.m. (CF_2); $J_{2a,3}$ 23·4, $J_{2b,3}$ 4·8 Hz, *m/e* 352 (M^+, 15%), 333 [$(M - F)^+$, 20%], 283 [$(M - CF_3)^+$, 100%], and 233 [$(M - C_2F_5)^+$, 15%], $\nu_{max.}$ 1615, 1436, 1340, 1215, 1120, 1110, 968, and 755 cm^{-1}, $\lambda_{max.}$ 269 (ε 3860) and 264infl nm (3710); and component B, *perfluoro-4,5-diethylpyrimidine*, b.p. 129—130° (Found: C, 27·5; N, 8·3; F, 64·4. $C_8F_{12}N_2$ requires C, 27·3; N, 7·95; F, 64·8%), ^{19}F δ 35·9 (F-2), 41·0 (F-6), 81·0 and 83·9 (CF_3's), and 108·4 p.p.m. (CF_2's), *m/e* 352 (M^+, 5%), 333 [$(M - F)^+$, 30%], 283 [$(M - CF_3)^+$, 100%], and 233 [$(M - C_2F_5)^+$, 60%], $\nu_{max.}$ 1580 and 1618 cm^{-1}, $\lambda_{max.}$ 248·5 (ε 2500).

At 790° under vacuum conditions, a gas chromatogram of the pyrolysis products from perfluoro-4,5-diethylpyridazine showed the same peaks, although that due to the starting pyridazine accounted for *ca.* 60% of the mixture.

Pyrolysis of Perfluoro-4-ethylpyridazine.—Perfluoro-4-ethylpyridazine (1·3 g) was pyrolysed by passing the vapour in a stream of dry N_2 through a platinum-lined silica tube packed with platinum foil at 700° (contact time *ca.* 55 s). Analysis (g.l.c. and ^{19}F n.m.r.) indicated the liquid pyrolysate (0·9 g) to contain perfluoro-4-ethylpyridazine (15%) and two other components (50 and 35%). Preparative scale g.l.c. (trixylenyl phosphate on Celite) yielded pure samples of (i) *perfluoro-5-ethylpyrimidine* (major product) (Found: C, 28·8; N, 11·3. $C_6F_8N_2$ requires C, 28·6; N, 11·1%), ^{19}F δ 34·8 (F-2), 47·4 (F-4), 86·0 (CF_3), and 112·7 p.p.m. (CF_2), $J_{4,5a}$ 25, $J_{4,5b}$ 6·5, $J_{5a,5b}$ 2 Hz, *m/e* 252 (M^+, 4%), 233 [$(M - F)^+$, 8%], and 183 [$(M - CF_3)^+$, 100%], $\lambda_{max.}$ 230 nm (ε 3830), $\nu_{max.}$ 1654, 1616, 1583, 1431, 1278, 1220, 1115, 1080, 1056, 965, and 800 cm^{-1}; and (ii) *perfluoro-4-ethylpyrimidine* (Found: C, 28·9; N, 11·5. $C_6F_8N_2$ requires C, 28·8; N, 11·1%), ^{19}F δ 44·8 (F-2), 69·0 (F-6), 83·6 (CF_3), 117·0 (CF_2), and 152·0 p.p.m. (F-5), $J_{2,5}$ 29, $J_{4a,4b}$ 1·5, $J_{4a,5}$ 23, $J_{4b,5}$ 6·1, $J_{5,6}$ 20 Hz, *m/e* 252 (M^+, 40%), 233 [$(M - F)^+$, 15%], and 183 [$(M - CF_3)^+$, 100%], $\lambda_{max.}$ 257·5 nm (ε 4000), $\nu_{max.}$ 1650w, 1620, 1594, 1478, 1422, 1335, 1220, 1165, 1051, 1042, 861, and 744 cm^{-1}.

Pyrolysis of Perfluoro-4-isopropylpyridazine.—Perfluoro-4-isopropylpyridazine (2·4 g) was passed in a stream of dry N_2 through a silica tube loosely packed with silica wool at 640° (contact time *ca.* 100 s). The gas chromatogram of the product (1·6 g) showed two major components, A (30%) and B (50%) in order of increasing retention time. Preparative scale g.l.c. (silicone elastomer) provided pure samples. Component A was shown by mass spectrometry and ^{19}F n.m.r. to be a 2 : 3 mixture of perfluoro-4- and -5-ethylpyrimidine (identified in the previous experiment). The mass spectrum of component B showed a parent peak at *m/e* 302 and ^{19}F n.m.r. indicated a 1 : 1 mixture of perfluoro-4-isopropylpyrimidine, δ (Me_2CO) 47·8 (F-2), 69·2 (F-6), 75·8 [$(CF_3)_2CF$], 152·8 (F-5), and 187·1 p.p.m. [$(CF_3)_2CF$], in agreement with published data,[11] and perfluoro-5-isopropylpyrimidine, δ (Me_2CO) 39·6 (F-2), 47·6 (F-4 and -6), 77·1 [$(CF_3)_2CF$], and 182·3 p.p.m. [$(CF_3)_2CF$].

Synthesis of Perfluoro-4,5-diethyl-3,6-di-isopropylpyridazine.—Perfluoro-4,5-diethylpyridazine (2·1 g, 6·0 mmol) and dry caesium fluoride (4 g) in tetramethylene sulphone (15 ml) were stirred at 80° in a carefully dried system for 2 h under hexafluoropropene (15 g, 100 mmol) at atmospheric pressure. The mixture was cooled, and volatile material removed *in vacuo* at room temperature. On warming to 80°, vacuum transfer yielded a pale yellow solid, *perfluoro-4,5-diethyl-3,6-di-isopropylpyridazine* (2·9 g, 75%), m.p. 79—80° (from CCl_4) (Found: C, 25·5; N, 4·5; F, 69·4. $C_{14}F_{24}N_2$ requires C, 25·75; N, 4·3; F, 69·95%), ^{19}F δ (Me_2CO) 69·5 (CF_3·CF_2), 70·6 [$(CF_3)_2CF$], 83·8 (CF_2), and 178·5 p.p.m. [$(CF_3)_2CF$], *m/e* 652 (M^+, 100%) and 633 [$(M - F)^+$, 50%], $\lambda_{max.}$ 267 (ε 900) and 365 nm (150), $\nu_{max.}$ 1500, 1251, 1231, 1205, 1170, 1141w, 1122, 1109, 1044, 1021, and 978 cm^{-1}.

Pyrolysis of Perfluoro-4,5-diethyl-3,6-di-isopropylpyridazine.—The pyridazine (2·0 g) was sublimed through a silica tube loosely packed with silica wool and heated to 650° over *ca.* 25 cm (backing pressure *ca.* 0·01 mmHg). A gas chromatogram of the product (1·6 g) showed a major peak of short retention time, several small peaks, and a significant peak of longer retention time. Preparative g.l.c. furnished pure samples of the two major products, the

short retention time component being *perfluoro-5-methylhex-3-yne* (320 mg); elemental analysis of this volatile liquid did not give consistent results, but all the spectral data are in agreement with the assigned structure: ^{19}F δ 78·6 [$(CF_3)_2CF$], 87·5 ($CF_3{\cdot}CF_2$), 107·8 (CF_2), and 170·6 p.p.m. [$(CF_3)_2CF$], $J_{1,2}$ 3·2, $J_{5,6}$ 9·8 Hz, *m/e* 312 (M^+, 0·5%), 293 [$(M - F)^+$, 25%], 243 [$(M - CF_3)^+$, 95%], and 69 (CF_3^+, 100%), $\nu_{max.}$ (Raman) 2278 cm^{-1}, $\nu_{max.}$ (i.r.; gas) 2285w, 1351, 1334, 1312, 1290, 1255, 1220, 1200, 1162, 1105, 1040, 985, 900, 795w, 763, 732, and 698 cm^{-1}. The second component (280 mg) was identical (i.r., n.m.r., and g.l.c.) with perfluoro-5,6-diethyl-2,4-di-isopropylpyrimidine prepared in the following experiment.

Synthesis of Perfluoro-5,6-diethyl-2,4-di-isopropylpyrimidine.—Perfluoro-4,5-diethylpyrimidine (1·6 g) and caesium fluoride (3·5 g) in tetramethylene sulphone (15 ml) were stirred at 70° in a carefully dried system for 1·5 h under an excess of hexafluoropropene (15 g); a bladder was used to maintain the system at atmospheric pressure. After complete uptake of gas, the mixture was cooled, and a volatile fraction consisting of dimers and trimers of hexafluoropropene was removed by vacuum transfer at room temperature. On warming, a second fraction (3·4 g) was obtained consisting mainly of a longer retention time component (g.l.c.) together with further oligomers of hexafluoropropene. Preparative scale g.l.c. gave *perfluoro-5,6-diethyl-2,4-di-isopropylpyrimidine* (1·45 g) (Found: C, 25·4; N, 4·25; F, 70·4. $C_{14}F_{24}N_2$ requires C, 25·75; N, 4·3; F, 69·95%), ^{19}F δ 72·6 (4b), 73·2 (5b), 76·4 (2b), 81·0 (6b), 89·9 and 112·0 (5a and 6a), 179·8 (4a), and 184·8 p.p.m. (2a), $J_{2a,2b}$ 6·7 Hz, *m/e* 652 (M^+, 25%), 633 [$(M - F)^+$, 64%], and 583 [$(M - CF_3)^+$, 100%], $\lambda_{max.}$ 251·5 nm (ε 1815).

Vacuum Pyrolysis of Perfluoro-4,5-di-isopropylpyridazine.—Perfluoro-4,5-di-isopropylpyridazine (5·30 g) was sublimed through a silica tube packed with silica wool and heated to 750° over 27 cm (backing pressure *ca.* 0·04 mmHg). A gas chromatogram of the product (2·93 g) showed it to contain the pyrazine (III) (4%), the pyrimidine (II) (15%), and three other major components, in order of retention time: A 31%, B 11%, and C 8%. Preparative scale g.l.c. (di-isodecyl phthalate on Chromosorb P) gave pure samples of components A—C; A was identified as *perfluoro-5,6-dimethylcyclobuta*[d]*pyridazine* (XXI) (Found: C, 31·0. $C_8F_{10}N_2$ requires C, 30·6%), ^{19}F δ (Me_2CO) 77·8 (CF_3), 81·0 (1,4-F), and 162·5 p.p.m. (tertiary F), *m/e* 314 (M^+, 100%), 295 [$(M - F)^+$, 38%], and 245 [$(H - CF_3)^+$, 50%], $\lambda_{max.}$ 263 and 329 nm, $\nu_{max.}$ 1755, 1600, 1440, 1352, 1302, 1220, 1172, 1070, 1002, 851, 813, 734, and 683 cm^{-1}. Component B was shown by mass spectrometry and ^{19}F n.m.r. to be an inseparable mixture of two compounds, one an isomer of (XXI) [^{19}F δ (Me_2CO) 77·1 (CF_3), 83·0 (1,4-F), and 161·8 p.p.m. (tertiary F)], and the other having structure (XXIII) [^{19}F δ (Me_2CO) 60·5 (5b-F_3), 69·3 and 69·6 (5b-F_2), 79·5 (3-F), 82·1 (6-F) (the 3- and 6-F signals can be assigned by examination of fine structure), 85·4 (4b-F_3), and 113·7 p.p.m. (4a-F_2)]. Component C was identified as perfluoro-4-ethyl-5-vinylpyridazine (XXII) (analysis gave inconsistent results), *m/e* 314 (M^+, 100%), 295 [$(M - F)^+$, 19%], and 245 [$(M - CF_3)^+$, 44%], ^{19}F δ (Me_2CO) 80·5 (3-F), 83·0 (6-F), 85·2 (4b-F_3), 95·5 and 109·7 (5b-F_2), 115·2 (4a-F_2), and 170·3 p.p.m. (4a-F), $\lambda_{max.}$ 273, 285, 298, and 337, $\nu_{max.}$ 1786, 1420, 1333, 1220, 1163, 1143, 1098, 1033, 914, 843, 758, and 726 cm^{-1}.

Flow Pyrolysis of Perfluoro-4,5-di-isopropylpyridazine.—The flow pyrolyses reported earlier [2] were repeated, using a platinum-coated silica tube filled with platinum foil as the reactor. The pyridazine was passed through the tube, in nitrogen, at a vapour pressure of *ca.* 0·3 atm (contact times 15—60 s).

At 530°, contact time *ca.* 40 s, a 75% recovery of non-gaseous product was achieved and this contained mostly starting material and the pyrimidine (II) (*ca.* 30% of the product).

At 580°, *ca.* 60 s contact time, the recovery was 50% and the product contained *ca.* 80% of the pyrimidine (II), starting material, and a trace of the pyrazine (III).

At 600°, *ca.* 30 s contact time, the recovery was 65% and the product contained *ca.* 65% of the pyrimidine (II), starting material (*ca.* 10%), and the pyrazine (III) (*ca.* 10%).

At 630°, *ca.* 30 s contact time, the recovery was 40% and the product contained a negligible amount of starting material, the pyrimidine (II) (*ca.* 20%), the pyrazine (III) (*ca.* 35%), and several unidentified components which were not seen at lower temperatures.

The foregoing quantitative analyses are based on g.l.c. traces and therefore subject to error. In particular, isolation of the pyrazine (III) by preparative g.l.c. from some of the pyrolysis experiments, followed by n.m.r. examination, revealed that the pyrazine (III) contained minor impurities not distinguishable by g.l.c.

Pyrolysis of the pyrimidine (II) at 630° gave no pyrazine (III) and the pyrimidine was largely recovered; pyrolyses at higher temperatures led to increasing amounts of decomposition of the pyrimidine.

Static Pyrolysis of Perfluoropyridazines.—Perfluoro-4,5-di-isopropylpyridazine (10 g) in a sealed nickel tube flushed with dry nitrogen was heated to 370° for 16 h. On cooling, the tube was opened and the contents were vacuum transferred (at 0·05 mmHg) into a trap cooled in liquid air. The contents of the trap (9·2 g) showed a trace of starting material on g.l.c. and only one product. This product, *perfluoro-4,5-di-isopropylpyrimidine* (II), was purified by fractional distillation at atmospheric pressure, the fraction distilling between 148 and 150° being collected; this was a clear white liquid which did not fume or undergo spontaneous hydrolysis and gave i.r. and ^{19}F n.m.r. spectra (acetone solution) identical with those recorded for (II), previously given the structure (IIa), obtained from flow pyrolysis experiments.[2] The pure liquid gave an improved ^{19}F n.m.r. spectrum permitting a different assignment [see (XVI) for atom designations]: ^{19}F δ 36·2 (s, 2-F), 34·9 (sept, 6-F), 70·1 (d, 4b-F_3), and 71·9 p.p.m. (dd, 5b-F_3). The 5a- and 4a-F signals appear as a quartet of septets, δ *ca.* 170·3, the outer signals being very weak. These signals were analysed by running a spectrum at a different field strength, which gave ^{19}F δ 168·1 (dsept, 4a- or 5a-F) and 172·6 p.p.m. (dsept, 5a- or 4a-F), $J_{4a,4b} = J_{5a,5b} = 10$ Hz, $J_{4a,5b}$ 185 Hz, $J_{5a,6}$ 27 Hz. This spectrum does not change over the temperature range 40—120°.

When the pyridazine (I) was heated in a sealed tube at 300°, the conversion into the pyrimidine (II) was *ca.* 20% in 24 h.

Perfluoro-3,5-di-isopropylpyridazine, perfluoro-3,4,6-tri-isopropylpyridazine, and perfluorotetraphenylpyridazine were unchanged under the foregoing conditions, at temperatures up to 380°

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