Photochemistry of Halogenocarbon Compounds. Part I.[1] Rearrangement of Pyridazines to Pyrazines

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Vapour phase irradiation of tetrafluoropyridazine and various perfluoroalkylpyridazines using either medium or low pressure mercury lamps gives pyrazine derivatives. Substituents located 4,5- and 3,5- in the pyridazine occur at 2,5- and 2,6-positions respectively in the resulting pyrazine, and a mechanism to accommodate these specific substituent labelling results is advanced which involves intermediate valence isomers. Perfluoro-2,5- and -2,6-di-isopropylpyrazines are very slowly interconverted by irradiation in the liquid phase.

IT has now become clear that, because of the greater strengths of C–F than C–H bonds, fluorine or fluorocarbon groups are useful as 'passive' substituents in systems where reactions or rearrangements of the skeleton of the molecule are being investigated. Earlier work from these laboratories led to the synthesis of tetrafluoropyridazine [2] and perfluoroalkylpyridazines [3,4]
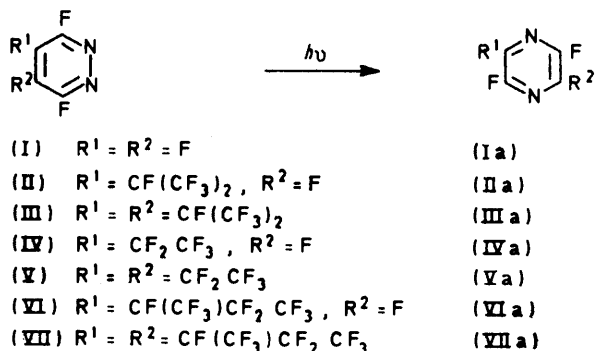
[1] Preliminary communication, C. G. Allison, R. D. Chambers, Yu. A. Cheburkov, J. A. H. MacBride, and W. K. R. Musgrave, Chem. Comm., 1969, 1200.

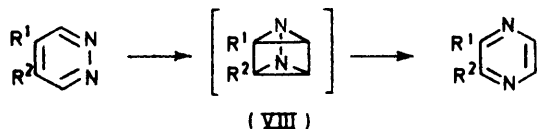[2] R. D. Chambers, J. A. H. MacBride, and W. K. R. Musgrave, J. Chem. Soc. (C), 1968, 2116.

[3] S. L. Bell, R. D. Chambers, M. Y. Gribble, and J. R. Maslakiewicz, J.C.S. Perkin I, 1973, 1716, and references therein.

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and, as described elsewhere, we have been concerned with the possibility of eliminating nitrogen from these systems by thermal or photochemical means.[5-7] Thermal elimination of nitrogen from pyridazines occurs in special cases,[6,7] but pyrolysis of fluorinated pyridazines has generally led to novel 1,2-shifts in the relative position of the nitrogen atoms and, likewise, nitrogen elimination did not occur on photolysis. Here we describe 1,3-shifts which take place on photolysis of tetrafluoropyridazine and some perfluoroalkylpyridazines.

(I)	$R^1 = R^2 = F$		(Ia)
(II)	$R^1 = CF(CF_3)_2$,	$R^2 = F$	(IIa)
(III)	$R^1 = R^2 = CF(CF_3)_2$		(IIIa)
(IV)	$R^1 = CF_2CF_3$,	$R^2 = F$	(IVa)
(V)	$R^1 = R^2 = CF_2CF_3$		(Va)
(VI)	$R^1 = CF(CF_3)CF_2CF_3$,	$R^2 = F$	(VIa)
(VII)	$R^1 = R^2 = CF(CF_3)CF_2CF_3$		(VIIa)

A series of perfluorinated pyridazines (I)—(VII) have been photolysed in sealed tubes (silica and Pyrex) using low and medium pressure mercury lamps. In each case the product contained the corresponding pyrazines (Ia)—(VIIa) in very high yield, except in the rearrangement of tetrafluoropyridazine, which was accompanied by some decomposition. There are a number of examples in the literature of photochemically induced 1,2-shifts in the relative position of substituents in benzenes,[8-14] and rearrangement of pyrazines to pyrimidines has also been reported,[15] but to our knowledge, when the rearrangement of fluorinated pyridazines was discovered[1] there was no reported case of a corresponding 1,3-shift in an aromatic system. The most obvious mechanism for rearrangement of a

(VIII)

pyridazine to a pyrazine involves a diazaprismane intermediate (VIII) and we tentatively suggested such a process in a preliminary communication.[1] Nevertheless,

it is clear that in such a process, the relative positions of substituents R^1 and R^2 should remain unchanged and, clearly, the direct formation of (IIIa), (Va), and (VIIa) from (III), (V), and (VII) respectively appears to rule out this mechanism. Initially, we suggested that (IIIa) might be produced *via* a fluoride-ion induced migration of perfluoroisopropyl groups[1] but we have since shown that such a rearrangement would be highly unlikely for pentafluoroethyl groups[16] and, therefore, this explanation could not account for the structure (Va). Furthermore, the conversion of the perfluoro-3,5-dialkylpyridazines (IX) and (X) into the corresponding pyrazines (IXa) and (Xa) rules out the possibility of equilibration involving anionic migration of perfluoro-isopropyl or -s-butyl groups and, therefore, the diazaprismane mechanism is completely eliminated. Also, Lemal and his co-workers[17] have rearranged 4,5-dichlorodifluoropyridazine to 2,5-dichlorodifluoropyrazine and reached a similar conclusion.

The results of these substituent labelling experiments now pose a fascinating mechanistic problem, *i.e.* we are effectively required to rotate the top half of the molecule (XI) through 180° with respect to the lower half. Substituents starting in the 4- and 5-positions in (XI) become *para* to each other in the pyrazine (XII), while 3- and 5-substituents in (XI) become *meta* to each other

| (IX) | $R = CF(CF_3)_2$ | (IXa) |
| (X) | $R = CF(CF_3)CF_2CF_3$ | (Xa) |
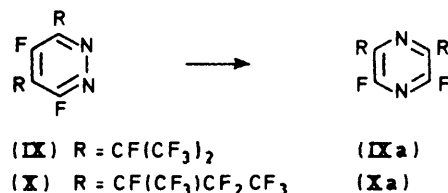
in (XII). All these requirements can, in fact, be met by a process which involves formation of a *para*-bonded species (XIII), followed by rearrangement, separation of the nitrogen atoms to give (XIV), and subsequent rearomatisation to (XII). We cannot envisage any other mechanism which embodies this high substituent specificity, which is itself a strong argument for the process, and, furthermore, we have now isolated intermediates[18,19] corresponding to both (XIII) and (XIV), which establishes the mechanistic path completely. Valence isomers of fluorinated pyridines have also been isolated.[20]

The rearrangement is not general for pyridazines and, comparing samples under identical conditions, it was

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

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[8] K. E. Wilzbach, A. L. Harkness, and L. Kaplan, *J. Amer. Chem. Soc.*, 1968, **90**, 1116.

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[16] R. D. Chambers and M. Y. Gribble, *J.C.S. Perkin I*, 1973, 1405.

[17] D. W. Johnson, V. Austel, R. S. Feld, and D. M. Lemal, *J. Amer. Chem. Soc.*, 1970, **92**, 7505.

[18] R. D. Chambers, W. K. R. Musgrave, and K. C. Srivastava, *Chem. Comm.*, 1971, 264.

[19] R. D. Chambers, J. R. Maslakiewicz, and K. C. Srivastava, *J.C.S. Perkin I*, in the press.

[20] M. G. Barlow, R. N. Haszeldine, and J. G. Dingwall, *J.C.S. Perkin I*, 1973, 1542.

significantly easier to rearrange perfluoro-4,5-di-iso-propylpyridazine (III) than the corresponding 3,5-isomer
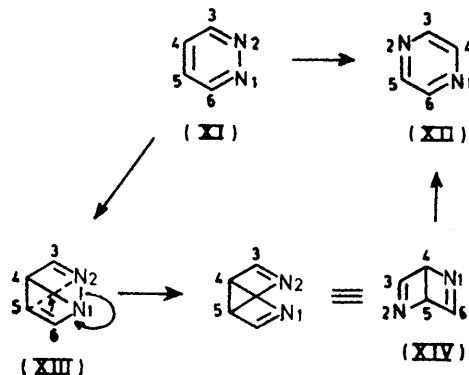
(IX). Furthermore, we have been unable to rearrange perfluoro-3,4,6-tri-isopropylpyridazine, perfluorotetra-phenylpyridazine, and various perfluoroalkylphenyl derivatives with substituents in either the 4,5- or ortho-positions; also we and others [17] have observed that perfluorotetraethylpyridazine is similarly inert.

The u.v. spectra of various fluorinated pyridazines are contained in the Table and there is no obvious

U.v. spectra of pyridazines (cyclohexane)

Substituents	$\lambda_{max.}/nm$ (ε)	
	$\pi \longrightarrow \pi^*$	$n \longrightarrow \pi^*$
H$_4$	246 (1400)	334 (360)
F$_4$ (I)	248 (4160)	283 (900)
4-CF(CF$_3$)$_2$, F$_3$ (II)	262 (1920)	313 (250)
4,5-CF(CF$_3$)$_2$, F$_2$ (III)	278 (4100)	340 (370)
3,5-CF(CF$_3$)$_2$, F$_2$ (IX)	256 (1940)	325 (270)
3,4,6-CF(CF$_3$)$_2$, F	255 (1940)	326 (240)
4-CF$_2$CF$_3$, F$_3$ (IV)	262 (2580)	312 (330)
4,5-CF$_2$CF$_3$, F$_2$ (V)	278 (4990)	349 (410)
3,4,5-CF$_2$CF$_3$, F	266 (2720)	346 (410)
(CF$_2$CF$_3$)$_4$	260 (980)	356 (240)
4-CF(CF$_3$)C$_2$F$_5$, F$_3$ (VI)	261 (2880)	306 (360)
4,5-CF(CF$_3$)C$_2$F$_5$, F$_2$ (VII)	277 (8060)	338 (770)
3,5-CF(CF$_3$)C$_2$F$_5$, F$_2$ (X)	257 (2820)	325 (360)

relationship between the u.v. spectra and ease of re-arrangement. The differing effects of perfluoroalkyl groups in the 4,5- and 3,6-positions are particularly puzzling. Replacing a fluorine atom at the 4- or 5-positions by fluoroalkyl leads to a bathochromic shift whereas the same substituents at the 3- or 6-positions lead to a small hyposochromic shift. There is no indication of steric effects causing differences between the various perfluoroalkyl compounds, even though the steric requirements of these groups vary substantially, and we suggest that the shifts arise from a stabilising influence of perfluoroalkyl groups on the highest oc-cupied molecular orbital and the lowest unoccupied orbital. For this explanation to be valid, the latter must be more important but, for substituents at the 3- and 6-positions, the effect would not operate because there are nodes for the lowest unoccupied orbital at these positions. The effect of replacing fluorine by a perfluoroalkyl group in any position, on the $n \rightarrow \pi^*$ transition is a bathochromic shift, with the effect being greater for the 4,5-positions. In summary, therefore,

although there is a difference in effect on the $\pi \rightarrow \pi^*$ transitions for perfluoroalkyl groups at the 4,5- vs. 3,5-positions, it is by no means clear that this is con-cerned with the ease of rearrangement.

In common with a number of other photochemically induced aromatic rearrangements,[11,21] the reactions described above do not appear to involve triplet states since added oxygen had no obvious effect on the reactions. Also, experiments in which mercury was rigorously excluded, gave results analogous to those with added mercury, ruling out the possibility that these are mercury sensitised. In the pure state tetrafluoro-pyrimidine and -pyrazine, as well as various perfluoro-alkyl derivatives, were photochemically stable, in the vapour phase, for extensive periods of u.v. radiation.

However, on irradiation of the liquid phase, rearrange-ment of perfluoro-2,5-di-isopropylpyrazine (IIIa) oc-curred very slowly giving a small amount of the isomer (IXa); pyrimidine (XVI) was also detected but this
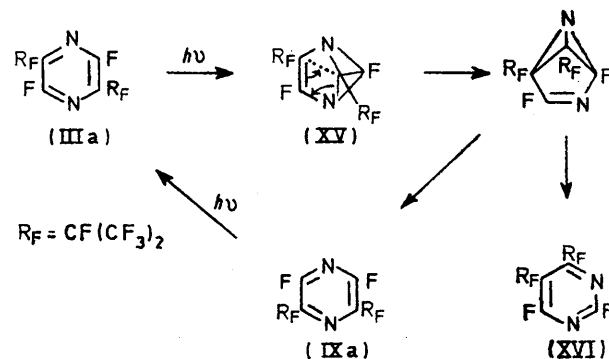
result was not consistently reproducible. Furthermore, a small amount of (IIIa) was produced from (IXa) on prolonged irradiation. These 1,2-shifts could be ex-plained by formation and rearrangement of diazabenz-valenes, similar to the mechanism which we suggested to account for specific substituent labelling in pyrolysis of pyridazines,[5,7] although no diazabenzvalenes have, so far, been isolated. It should be emphasised, how-ever, that rearrangements of pyrazines (IIIa) and (IXa) occur very much more slowly than the rearrange-ments of pyridazines to pyrazines described earlier and only in the liquid phase.

In earlier work [5,7] we showed that pyrolysis of fluorin-ated pyridazines gives mainly pyrimidines (as well as some pyrazines), i.e. 1,2-shifts, whereas we have now established that photolysis gives pyrazines, i.e. 1,3-shifts, and it is obvious to turn to orbital symmetry rules for an explanation of this difference. However, it is clear from the literature [22] that the rules do not account adequately for many observations concerning even benzene derivatives; the thermal 1,2-shifts in pyrid-azines which we have reported presumably occur via vibrationally excited ground states and the photo-

[21] I. Haller, J. Chem. Phys., 1967, 47, 1117.

[22] See, e.g., H. G. Barlow, R. N. Haszeldine, and R. Hubbard, J. Chem. Soc. (C), 1970, 1231, and references therein.

chemical 1,3-shifts almost certainly occur *via* the first excited states, but the basis for the different behaviour of fluorinated pyridazines on photolysis and pyrolysis has yet to be established.

As indicated earlier, photochemically initiated 1,3-shifts in aromatic systems are rare; *o*-xylene gives *p*-xylene but at wavelengths greater than 230 nm this almost certainly involves two 1,2-shifts although at shorter wavelengths a direct 1,3-shift may be involved.[9] Recently, shifts of methyl between the 4- and 2-positions and between 3- and 5-positions in methylpyridines have been reported[23] although in very low yield, and an azaprismane mechanism has been advanced. A mechanism analogous to that which we have now firmly established for the pyridazine system, accounts for the shifts more satisfactorily because this process allows interconversion between 2-, 6-, and 4-positions whereas an azaprismane mechanism[23] would also allow a methyl to shift from the 3- to the 2-position. Furthermore, other workers[24] have trapped a *para*-bonded species by '*in situ*' reduction. In contrast, however, azaprismanes have been suggested[25] to account for other 1,3-shifts in pyridines which our new mechanism would not explain.
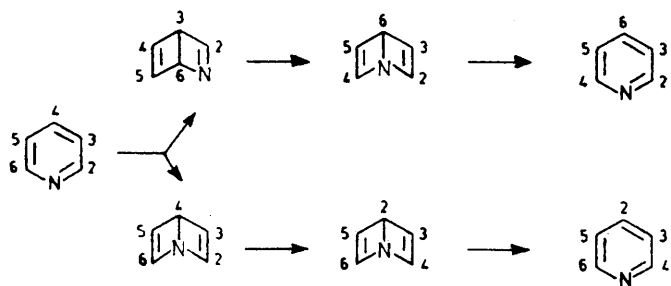
Structure Assignments of Fluorinated Pyrazines.— Perfluoro-2,5-di-isopropylpyrazine (IIIa) is a known compound[5] and ^{19}F substituent chemical shifts for introduction of the perfluoroisopropyl group into the pyrazine system may be deduced from this compound as well as from perfluoroisopropylpyrazine (IIa). Compound (IXa) is then easily distinguished from the alternative, perfluoro-2,3-di-isopropylpyrazine, on the basis of chemical shift of the ring fluorine atoms and their coupling with $CF(CF_3)_2$. The calculated value (68 p.p.m.) agrees with the observed value (66 p.p.m.) for (IXa) and these differ from the calculated values for the 2,3-isomer (83 p.p.m.). Analogous arguments, based on substituent chemical shifts derived from the corresponding perfluoroalkylpyrazines, may be used to demonstrate the structures of the perfluorodialkyl-pyrazines (Va), (VIIa), and (Xa). Compound (VIIa) was also obtained by direct polyfluoroalkylation[4,16] of tetrafluoropyrazine, using octafluorobut-2-ene.

EXPERIMENTAL

Unless otherwise stated reactions involved irradiation of the vapour phase, and were carried out using a Hanovia

U.V.S. 1000 medium pressure mercury arc at a distance of *ca.* 10 cm. The temperature in the irradiation zone was *ca.* 60 °C. Irradiations at 253·7 nm were carried out employing silica tubes and using low pressure mercury lamps within a Rayonet R.P.R.-208 reactor (Southern New England Ultraviolet Company) and the temperature within the irradiation zone was *ca.* 40 °C.

[19]F N.m.r. spectra were recorded on a Varian A56/60D spectrometer ($CFCl_3$ as external reference); all shifts are quoted relative to $CFCl_3$ (upfield shifts are quoted as positive).

Irradiations in Silica.—The first two experiments are described in detail and subsequent experiments were carried out in an identical manner except where stated.

(a) *Tetrafluoropyridazine* (I). Tetrafluoropyridazine (I) (2·0 g) sealed under vacuum in a dry silica tube (*ca.* 45 ml) was irradiated for 6 days. Volatile material (1·7 g) was transferred under vacuum, leaving a tar, and was shown by g.l.c. (di-isodecyl phthalate) and [19]F n.m.r. to be a mixture of tetrafluoropyridazine[2] (I) (20%) and tetra-fluoropyrazine[26] (Ia) (80%).

(b) *Perfluoro-4-isopropylpyridazine* (II). Perfluoro-4-iso-propylpyridazine (II) (0·60 g) was sealed in a tube (29 × 320 mm) and irradiated for 66·5 h. The volatile product was shown by g.l.c. to be one component, identified as *perfluoro-2-isopropylpyrazine* (IIa) (0·55 g, 92%) (Found: C, 27·6; N, 9·4; F, 63·3%; M^+, 302. $C_7F_{10}N_2$ requires C, 27·8; N, 9·3; F, 62·9%; M, 302), [19]F δ 76·7 [$(CF_3)_2CF$], 78·0 (F-3), 83·7 (F-5), 93·4 (F-6), and 186·7 p.p.m. [$(CF_3)_2CF$].

(c) *Perfluoro-4,5-di-isopropylpyridazine* (III). Perfluoro-4,5-di-isopropylpyridazine (III) (1·50 g) was irradiated for 96 h. The volatile product was shown by g.l.c. to be one component which was identified as perfluoro-2,5-di-isopropylpyrazine (IIIa)[5] (1·15 g, 77%), by comparison of its [19]F n.m.r. and i.r. spectra with those of an authentic sample.

(d) *Perfluoro-4-ethylpyridazine* (IV). Perfluoro-4-ethyl-pyridazine (IV) (0·50 g) was irradiated for 144 h. The volatile product was shown by g.l.c. to be one component, identified as *perfluoro-2-ethylpyrazine* (IVa) (0·40 g, 80%) (Found: C, 28·2; F, 60·8%; M^+, 252. $C_6F_8N_2$ requires C, 28·55; F, 60·3; M, 252), [19]F δ 79·3 (F-3), 82·5 (F-5), 86·0 [CF_3CF_2], 93·5 (F-6), and 118·4 p.p.m. [CF_3CF_2].

(e) *Perfluoro-4,5-di-ethylpyridazine* (V). Perfluoro-4,5-diethylpyridazine (V) (0·45 g) was irradiated for 125 h. The volatile product (0·33 g) was shown by g.l.c. to contain two major components and preparative scale g.l.c. gave perfluoro-4,5-diethylpyridazine (V) (15 mg) and *perfluoro-2,5-diethylpyrazine* (Va) (0·20 g, 44·4%) (Found: C, 27·3; F, 64·5%; M^+, 352. $C_8F_{12}N_2$ requires C, 27·25; F, 64·75%; M, 352), [19]F δ 78·3 (F-3, 6), 85·4 [CF_3CF_2], and 119·0 p.p.m. [CF_3CF_2].

(f) *Perfluoro-4,5-di-s-butylpyridazine* (VIII). Perfluoro-4,5-di-s-butylpyridazine[4] (VII) (1·28 g) was irradiated for 144 h. The volatile product (0·75 g) was shown by g.l.c. (silicone elastomer) to contain only one major component, and preparative scale g.l.c. furnished perfluoro-2,5-di-s-butylpyrazine (VIIa) (0·60 g, 46·9%) (see later).

[23] S. Caplain and A. Lablache-Combier, *Chem. Comm.*, 1970, 1247.

[24] K. E. Wilzbach and D. J. Rausch, *J. Amer. Chem. Soc.*, 1970, **92**, 2178.

[25] T. J. van Bergen and R. M. Kellog, *J. Amer. Chem. Soc.*, 1972, **94**, 8451.

[26] C. G. Allison, R. D. Chambers, J. A. H. MacBride, and W. K. R. Musgrave, *J. Chem. Soc.* (C), 1970, 1023.

(g) *Perfluoro-3,5-di-isopropylpyridazine* (IX). Perfluoro-3,5-di-isopropylpyridazine (IX) (2·10 g) was irradiated for 115 h. The volatile product (1·80 g) was shown by g.l.c. (silicone elastomer) to contain one major component, and preparative scale g.l.c. gave *perfluoro-2,6-di-isopropylpyrazine* (IXa) (1·55 g, 74%) (Found: C, 26·3%; M^+, 452. $C_{10}F_{16}N_2$ requires C, 26·55%; M, 452), ^{19}F δ 66·2 (F-3, 5), 77·0 [$(CF_3)_2CF$], and 187·0 p.p.m. [$(CF_3)_2CF$].

(h) *Perfluoro-3,4,6-tri-isopropylpyridazine*. Perfluoro-3,4,6-tri-isopropylpyridazine (1·00 g) was irradiated for 67 h. Starting material (0·95 g) was recovered.

(i) *Perfluorotetraethylpyridazine*. Perfluorotetraethyl pyridazine (0·36 g) was irradiated for 205·5 h. The product (0·36 g), although discoloured, was unchanged starting material.

Irradiations in Pyrex.—(a) *Perfluoro-4,5-di-isopropylpyridazine* (III). Perfluoro-4,5-di-isopropylpyridazine (III) (0·6 g) was sealed under high vacuum (0·001 mmHg) in a dry Pyrex tube (34 × 320 mm) and irradiated for 90 h. The volatile product (0·55 g) was transferred under vacuum and a small amount of intractable tar remained. The former was shown by g.l.c. to be one component which was identified as perfluoro-2,5-di-isopropylpyrazine [5] by comparison of its i.r. and ^{19}F n.m.r. spectra with those of an authentic sample.

(b) *Perfluoro-3,5-di-isopropylpyridazine* (IX). Perfluoro-3,5-di-isopropylpyridazine (IX) (1·0 g) was irradiated for 143 h in a tube (34 × 320 mm). The volatile product (0·85 g) was shown by g.l.c. (silicone elastomer) to consist of starting material (IX) (5%) and perfluoro-2,6-di-isopropylpyrazine (IXa) (95%) which were identified by g.l.c. and by comparison of the ^{19}F n.m.r. spectrum of (IXa) with that of an authentic sample.

(c) *Tetrafluoropyridazine* (I). Tetrafluoropyridazine (I) (1·1 g) was irradiated for 112 h in a tube (34 × 320 mm). The volatile product (0·52 g) was shown by g.l.c. and by ^{19}F n.m.r. spectroscopy to be mainly starting material (I) (89%), with tetrafluoropyrazine (Ia) (11%).

Irradiation at 253·7 nm.—(a) *Perfluoro-4-s-butylpyridazine* (VI). Perfluoro-4-s-butylpyridazine (1·0 g) and CF_2ClCF_2Cl (33 ml) were sealed in a silica tube under high vacuum and irradiated at 253·7 nm for 330 h. Evaporation of solvent gave a pure (g.l.c.) oil (1·0 g) identified as *perfluoro-2-s-butylpyrazine* (VIa) (1·0 g, 100%) (Found: C, 27·0; N, 7·8; F, 64·3%; M^+, 352. $C_8F_{12}N_2$ requires C, 27·25; N, 7·95; F, 64·75%; M, 352), ^{19}F δ 75·0 [$CF_3(CF_3CF_2)CF$], 77·9 (F-3), 82·7 [$CF_3(CF_3CF_2)CF$], 84·2 (F-5), 95·3 (F-6), 122·2 [$CF_3(CF_3CF_2)CF$], and 187·6 p.p.m. [$CF_3(CF_3CF_2)CF$].

(b) *Perfluoro-3,5-di-s-butylpyridazine* (X). Perfluoro-3,5-di-s-butylpyridazine (X) (1·0 g, 1·81 mmol) dissolved in CF_2ClCF_2Cl (30 ml) was irradiated for 400 h under similar conditions to above. Solvent evaporation gave an oil (1·0 g) which was shown by g.l.c. to contain two components. Preparative scale g.l.c. gave starting matrial (X) and *perfluoro-2,6-di-s-butylpyrazine* (Xa) (67% yield, estimated by g.l.c.) (Found: C, 26·4; N, 5·4; F, 68·3%; M^+, 552. $C_{12}F_{20}N_2$ requires C, 26·1; N, 5·05; F, 68·85%; M, 552), ^{19}F δ 66·4 (F-3, 5), 74·9 [$CF_3(CF_3CF_2)CF$], 81·0 [$CF_3(CF_3CF_2)CF$], 122·2 [$CF_3(CF_3CF_2)CF$], and 188·5 p.p.m. [$CF_3(CF_3CF_2)CF$].

Irradiation of Perfluoro-4,5-di-isopropylpyridazine in the

Absence of Mercury.—A new silica tube (41 × 300 mm) containing perfluoro-4,5-di-isopropylpyridazine (III) (0·95 g) and gold foil (10 × 100 mm) was evacuated (0·075 mmHg) using a mercury-free vacuum system. An identical silica tube (41 × 300 mm) containing perfluoro-4,5-di-isopropylpyridazine (III) (1·00 g) and mercury (0·5 g) was evacuated (0·075 mmHg) using a vacuum system containing mercury. Both tubes were irradiated at 253·7 nm for 800 h under the same conditions and their products were identical by g.l.c., indicating that the rearrangement of pyridazines to pyrazines is not sensitised by mercury.

Synthesis of Perfluoro-2,5-di-s-butylpyrazine (VIIa) (*With* S. PARTINGTON).—A nickel tube containing a mixture of tetrafluoropyrazine (5·0 g, 33 mmol), caesium fluoride (6·0 g, 39·5 mmol), octafluorobut-2-ene (8·0 g, 40·0 mmol), and sulpholan (15 ml) was rotated in an oil-bath at 160° for 48 h. Volatile material was transferred from the tube under vacuum and then separated by distillation into tetrafluoropyrazine (1·2 g) and a liquid, identified as *perfluoro-2,5-di-s-butylpyrazine* (VIIa) (10 g, 55%), b.p. 165° at 760 mmHg (Found: C, 25·9; F, 68·3; N, 6·0%; M^+, 552. $C_{12}F_{20}N_2$ requires C, 26·1; F, 68·85; N, 5·05%; M, 552), ^{19}F δ 74·6 [$CF_3(CF_3CF_2)CF$], 76·7 (3,6-F), 82·5 [$CF_3(CF_3CF_2)CF$], 122·0 [$CF_3(CF_3CF_2)CF$], and 188·0 p.p.m. [$CF_3(CF_3CF_2)CF$].

Prolonged Irradiation of Perfluoro-4,5-di-isopropylpyridazine (III).—Perfluoro-4,5-di-isopropylpyridazine (III) (1·00 g) was sealed under high vacuum in a silica tube and irradiated for 800 h. The volatile product (0·80 g) was shown by g.l.c. to contain, in addition to pyrazine (IIIa) (*ca.* 75%), and starting material (III) (*ca.* 5%), another component (*ca.* 20%). Separation by preparative scale g.l.c. gave pure samples of each component. The unknown material was found by g.l.c. (silicone elastomer) to be a 1 : 1 mixture of two compounds, and preparative scale g.l.c. (silicone elastomer) furnished pure samples of perfluoro-2,6-di-isopropylpyrazine (IXa) (see above) and perfluoro-4,5-di-isopropylpyrimidine (XVI) [7] which were identified by comparison of their i.r. with those of authentic samples. This sequence of separation was necessary because pyrazines (IIIa) and (IXa) were not resolved by g.l.c. using silicone elastomer as stationary phase.

Irradiation of Perfluoro-2,5-di-isopropylpyrazine (IIIa).—Perfluoro-2,5-di-isopropylpyrazine (IIIa) (0·65 g) in the liquid phase was irradiated at 253·7 nm for 240 h. The product was found by g.l.c. to contain a minor product (*ca.* 3%) and starting material (IIIa). Examination by mass spectrometry–g.l.c. showed the minor product to be perfluoro-2,6-di-isopropylpyrazine (IXa). We were unable to determine whether any perfluoro-4,5-di-isopropylpyrimidine (XVI) [7] was present in the minor product.

Irradiation of Perfluoro-2,6-di-isopropylpyrazine (IXa).—Perfluoro-2,6-di-isopropylpyrazine (IXa) (0·55 g) in the liquid phase was irradiated at 253·7 nm for 240 h. The product was found by g.l.c. to contain a minor product (*ca.* 1%) which was identified as perfluoro-2,5-di-isopropylpyrazine (IIIa) by mass spectrometry–g.l.c. We were unable to determine whether any perfluoro-4,5-di-isopropylpyrimidine (XVI) was present in the product.