Polyfluoroheterocyclic Compounds. Part XXIV.[1] Thermal Elimination of Molecular Nitrogen from Polyfluoro- and Polychloro-pyridazines †

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Perfluorotetraphenylpyridazine and perfluorodialkyldiarylpyridazines have been synthesised by reaction of penta-fluorophenyl-lithium or tetrafluoro-4-pyridyl-lithium with tetrafluoropyridazine or perfluoro-4,5-dialkylpyridazines. Pyrolytic elimination of nitrogen from these pyridazines is described, giving the acetylenes $C_6F_5 \cdot C \equiv CR_F$ [$R_F = C_6F_5$, C_2F_5, or $(CF_3)_2CF$] and $(4-C_5F_4N)C \equiv CCF(CF_3)_2$. Pyrolysis of tetrachloropyridazine leads to a mixture of products arising from nitrogen elimination. Similarly perchlorocinnoline yields perchlorophenylacetylene, and perchloro-phthalazine gives tetrachlorophthalonitrile. These results suggest that nitrogen extrusion from pyridazines leads to diradical intermediates rather than cyclobutadienes or tetrahedral species.

THERMAL elimination of molecular nitrogen from systems like pyrazolines[2] is well known, whereas when this work began, corresponding eliminations from pyrid-azines had not been reported. Our earlier report of pyrolyses of perfluoroalkylpyridazines described re-

arrangements to pyrimidines and pyrazines, rather than loss of nitrogen.[3] However, we now report thermal reactions of some pyridazines where extrusion of molecular nitrogen is the dominant process.

The C_4 fragment obtained by loss of nitrogen could

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[1] Part XXIII, R. D. Chambers, D. T. Clark, T. F. Holmes, W. K. R. Musgrave, and I. Ritchie, preceding paper.

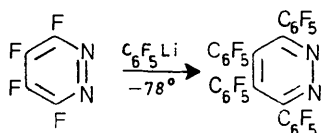[2] B. P. Stark and A. J. Duke, ' Extrusion Reactions,' Pergamon, Oxford, 1967.

[3] R. D. Chambers, J. A. H. MacBride, and W. K. R. Musgrave, J. Chem. Soc. (C), 1971, 3384.

have any of a variety of structures and we have been concerned to distinguish between the following possibilities: a diradical (A); a cyclobutadiene [4,5] (B); or even a tetrahedrane [5] (C).   Elimination of nitrogen is a
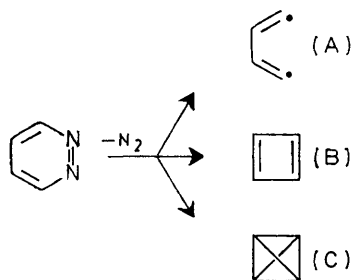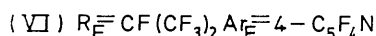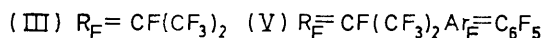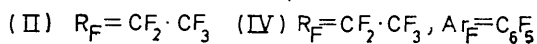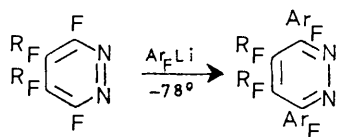

process which is apparent in the mass spectra of some pyridazines [3,6,7] and tetrahedral structures have been proposed for some fragments to account for deuterium scrambling in the mass spectra of substituted cyclopentadienols.[8]   Tetrahedrane and derivatives have been suggested as transient intermediates in other systems but the evidence remains inconclusive.[5,9-11]

We have now synthesised a series of perfluoroaryl derivatives of pyridazines [(I) and (IV)—(VI)] by reactions of pentafluorophenyl- or tetrafluoro-4-pyridyllithium with tetrafluoropyridazine or the perfluoroalkyl derivatives (II) [12] and (III).[13]   The formation of (I), involving ready direct tetrasubstitution in tetrafluoropyridazine, no doubt reflects both the reactivity of the lithio-derivative and the fact that polyfluoroaryl groups, as substituents, are strongly activating towards further nucleophilic substitution.[14]   This is in contrast to some

(I)

(II) $R_F = CF_2 \cdot CF_3$ (IV) $R_F = CF_2 \cdot CF_3$, $Ar_F = C_6F_5$

(III) $R_F = CF(CF_3)_2$ (V) $R_F = CF(CF_3)_2 \, Ar_F = C_6F_5$

(VI) $R_F = CF(CF_3)_2 \, Ar_F = 4 - C_5F_4N$

polyfluoroalkylation reactions where the higher steric requirements of polyfluoroalkyl groups and the re-

versibility of the process limits the degree of substitution.[15]   The reaction of tetrafluoropyridazine with 2 mol. equiv. of pentafluorophenyl-lithium gave a mixture containing perfluorotetraphenylpyridazine (I) and perfluoro-4,5-diphenylpyridazine; it was very difficult to limit further substitution.

Pyrolyses were carried out (a) using flow conditions in a stream of dry nitrogen, at atmospheric pressure, and (b) under vacuum.   The products were the same in both systems, except that a higher temperature was required to effect reaction in the vacuum procedure. Similar results were obtained whether the sample was contained in a silica tube packed with silica wool, or a platinum-lined silica tube packed with platinum foil.

Perfluorotetraphenylpyridazine (I) and the perfluoroalkylaryl derivatives (IV)—(VI), on pyrolysis, gave the

(I)	725° (VII)	X=Y=C_6F_5 (90%)
(IV)	720° (VIII)	X=CF_2CF_3, Y=C_6F_5 (88%)
(V)	680° (IX)	X=$CF(CF_3)_2$,Y=C_6F_5 (84%)
(VI)	700° (X)	X=$CF(CF_3)_2$,Y=4-C_5F_4N (82%)

acetylenes (VII)—(X) in excellent yields; this represents a novel route to some new perfluorinated acetylenes, which are in general not easily accessible.

We have been unable to detect any of the symmetrical acetylenes, e.g. XC≡CX, in the pyrolysis of compounds (IV)—(VI).   If an intermediate tetrahedrane, or possibly cyclobutadiene, had been involved, then we would have anticipated more random fission to produce symmetrical as well as unsymmetrical acetylenes.   The results are, therefore, much more consistent with the intermediacy of diradicals corresponding to (A) rather than cyclic structures (B) and (C).   There is, however evidence for the formation of cyclic structures in the mass spectrometer.   The base peaks from (IV) and (V) correspond to $[C_2F_5 \cdot C \equiv C \cdot C_6F_5 - CF_3]^+$ and $[C_3F_7 \cdot C \equiv C \cdot C_6F_5]^+$, respectively, but in each case there was a significant peak corresponding to $[C_6F_5 \cdot C \equiv C \cdot C_6F_5]^+$ (see Experimental section for percentages).   This clearly indicates a degree

[4] M. P. Cava and M. J. Mitchell, ' Cyclobutadiene and Related Compounds,' Academic Press, New York, 1967.
[5] L. T. Scott and M. Jones, Chem. Rev., 1972, 72, 181.
[6] S. J. Weininger and E. R. Thornton, J. Amer. Chem. Soc., 1967, 89, 2050.
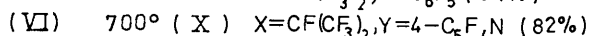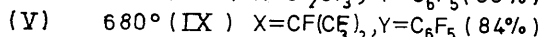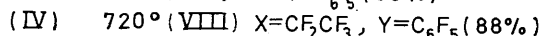[7] M. H. Benn, T. S. Sorensen, and A. M. Hogg, Chem. Comm., 1967, 574.
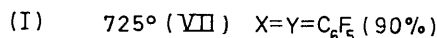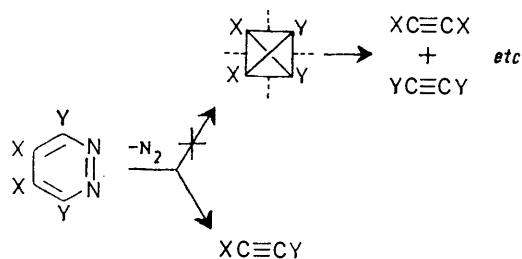[8] M. M. Bursey and T. A. Elwood, J. Amer. Chem. Soc., 1969, 91, 3812, and references therein.
[9] P. B. Shevlin and A. P. Wolf, J. Amer. Chem. Soc., 1970, 92, 406.

[10] R. F. Peterson, R. T. K. Baker, and R. L. Wolfgang, Tetrahedron Letters, 1969, 4749.
[11] L. B. Rodewald and Hak-Ki Lee, J. Amer. Chem. Soc., 1973, 95, 623.
[12] R. D. Chambers and M. Y. Gribble, J.C.S. Perkin I, 1973, 1405.
[13] R. D. Chambers, Yu. A. Cheburkov, J. A. H. MacBride, and W. K. R. Musgrave, J. Chem. Soc. (C), 1971, 532.
[14] R. J. de Pasquale and C. Tamborski, J. Org. Chem., 1967, 32, 2163.
[15] S. L. Bell, R. D. Chambers, M. Y. Gribble, and J. R. Maslakiewicz, J.C.S. Perkin I, 1973, 1716.

of scrambling which is only consistent with an intermediate ion derived from tetrahedrane or cyclobutadiene.

SCHEME
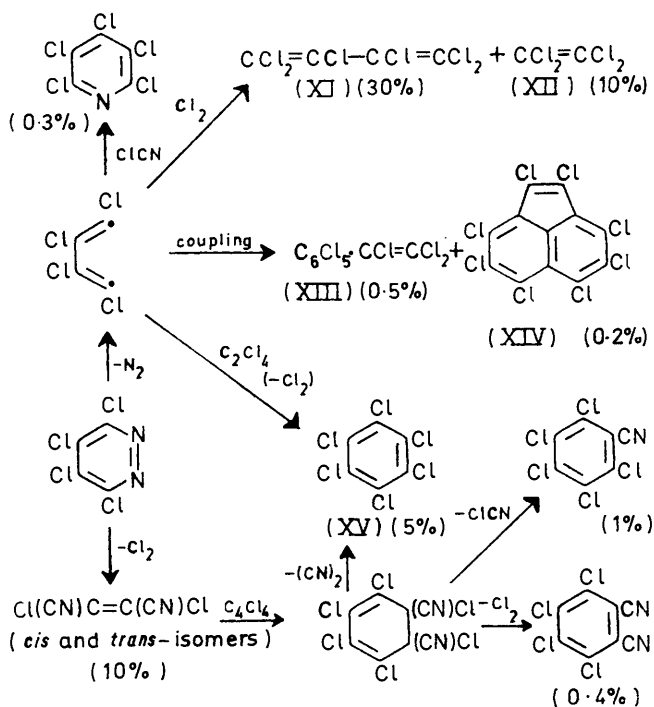
In contrast to tetrafluoropyridazine,[3] pyrolysis of tetrachloropyridazine proceeded with loss of nitrogen rather than rearrangement as the principal process. The product contained mainly hexachlorobutadiene and molecular chlorine, together with a variety of other compounds as shown in the Scheme. The compounds can be divided into two groups: (i) those which arise from an initial loss of nitrogen from tetrachloropyridazine, followed by combination of C_4Cl_4 fragments, and (ii) those formed by initial cleavage of the N–N bond in tetrachloropyridazine, followed by the reactions indicated.

The structure of the intermediate C_4Cl_4 fragment cannot be clearly defined on the basis of the products of combination, which were obtained in such low yield; nevertheless the formation of compounds (XI)—(XV) is more readily explained on the basis of a diradical (A) than a cyclobutadiene (B). The products obtained in these reactions differ considerably from those reported for the pyrolysis of tetrachloro-*ortho*-benzoquinone, where at 720° $CCl{\equiv}C{\cdot}CCl{=}CCl_2$ (60%) and $CCl{\equiv}C{\cdot}C{\equiv}CCl$ (1%) were isolated.[16] This suggests that loss of nitrogen from tetrachloropyridazine is the more difficult process, with corresponding increased competition from C–Cl bond fission to give molecular chlorine.

We have studied the pyrolysis of 4,5-dichlorodifluoro-

pyridazine,[17] a system from which we anticipated both nitrogen elimination and rearrangement. Complex mixtures were obtained, however, under a variety of conditions (840° with vacuum transfer or 620—780° with nitrogen flow), and we were unable to isolate any identifiable products. Reactions of perchlorobenzopyridazines showed two distinct processes. Perchlorocinnoline[18] (XVI) lost nitrogen on pyrolysis giving perchlorophenylacetylene (XVII) and not the corresponding benzocyclobutadiene (XVIII); this is consistent with the intermediacy of a diradical (XIX) and transfer of a chlorine atom. In contrast, perchlorophthalazine[19] (XX) lost chlorine on pyrolysis, giving tetrachlorophthalonitrile (XXI). The difference in behaviour of (XVI) and (XX) is probably a reflection of the greater stability of the diradical (XIX) than of the diradical (XXII). Indeed the bulk of evidence available from our results suggests the formation of diradical intermediates in these extrusion reactions. This is consistent with conclusions drawn from orbital symmetry considerations, that concerted nitrogen extrusion from pyridazines by either pyrolysis or photolysis is unfavourable.[20]
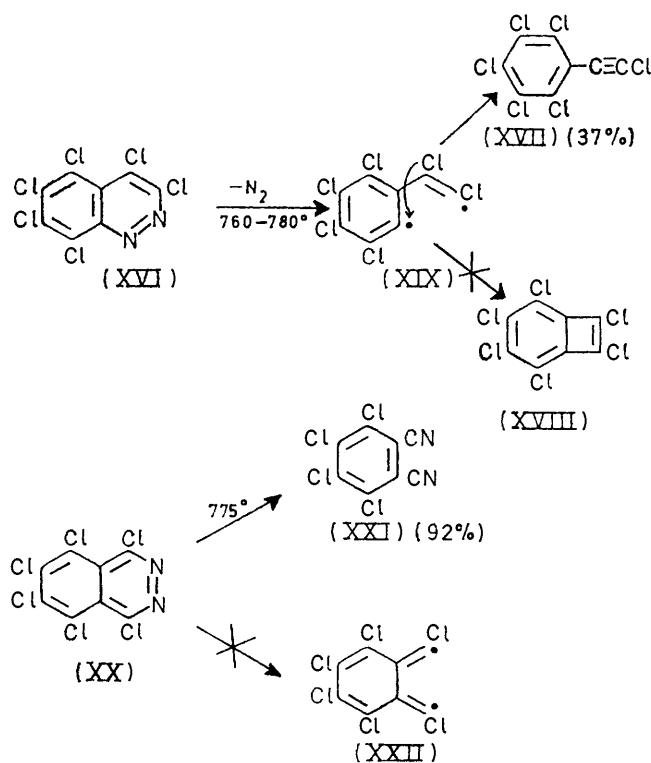
The examples described in this paper illustrate that elimination of nitrogen from pyridazines is not uncommon; an extension of this work has shown that benzo[c]cinnolines give biphenylenes.[21] Other workers[22]

[16] D. C. DeJongh, D. A. Brent, and R. Y. Van Fossen, *J. Org. Chem.*, 1971, **36**, 1469.

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

[18] R. D. Chambers, J. A. H. MacBride, and W. K. R. Musgrave, *Chem. Comm.*, 1970, 739.

[19] R. D. Chambers, J. A. H. MacBride, W. K. R. Musgrave, and I. S. Reilly, *Tetrahedron Letters*, 1970, 57.

[20] P. Beak and W. R. Messer, 'Organic Photochemistry,' ed. O. L. Chapman, Marcel Dekker, New York, 1969, vol. 2, p. 117.

[21] J. A. H. MacBride, *J.C.S. Chem. Comm.*, 1972, 1219.

[22] B. M. Adger, M. Keating, C. W. Rees, and R. C. Storr, *J.C.S. Chem. Comm.*, 1973, 19.

have described the elimination of nitrogen from 4-phenyl-1,2,3-benzotriazine; surprisingly, 2-phenylbenzazete was isolated.

EXPERIMENTAL

Because of the possibility of explosions,[23] all reactions involving organolithium compounds were conducted in a fume cupboard behind a blast screen in apparatus which had been baked in an oven and purged with dry nitrogen. Pentafluorophenyl-lithium was prepared from pentafluorobenzene and butyl-lithium (commercial solution in hexane) in ether–hexane (sodium-dried) at $-78°$, and tetrafluoropyridyl-lithium [24] was obtained from butyl-lithium and 4-bromotetrafluoropyridine in hexane at $-78°$.

^{19}F N.m.r. spectra were recorded on a Varian A56/60D spectrometer ($CFCl_3$ or C_6F_6 as internal reference); all shifts are quoted relative to $CFCl_3$ (upfield shifts are quoted as positive) even when hexafluorobenzene was the solvent ($\delta_{CFCl_3} = \delta_{C_6F_6} + 163.0$).

Perfluorotetraphenylpyridazine (I).—Tetrafluoropyridazine (6.0 g, 39.5 mmol) was added to pentafluorophenyl-lithium [from pentafluorobenzene (30 g, 179 mmol) and butyl-lithium] in ether–hexane (2 : 1) at $-78°$. The mixture was stirred for 1 h and then allowed to warm to room temperature overnight, before hydrolysis with dilute sulphuric acid. The mixture was extracted with methylene chloride (4×150 ml); evaporation of the extracts gave white crystals of *perfluorotetraphenylpyridazine* (25.2 g, 86%), m.p. 250—251° (from dichloromethane) (Found: C, 45.3; F, 50.9; N, 3.6. $C_{28}F_{20}N_2$ requires C, 45.2; F, 51.1; N, 3.8%), ^{19}F δ (Me_2CO) 140.6 (F-2), 149.2 (F-4), and 159.8 p.p.m. (F-3) for the 3- and 6-pentafluorophenyl groups, and 141.8 (F-2'), 150.9 (F-4'), and 161.3 (F-3') for the 4- and 5-pentafluorophenyl groups, m/e 744 (M^+, 50%), 716 [$(M - N_2)^+$, 6%], 358 ($C_{12}F_{10}^+$, 100%), and 289 ($C_{11}F_7^+$, 35%), $\lambda_{max.}$ 221 (log ϵ 4.25) and 246.5 nm (4.36), $\nu_{max.}$ 1657, 1502, 1448, 1373, 1114, 997, 940, and 855 cm^{-1}.

Perfluoro-4,5-diphenylpyridazine.— Tetrafluoropyridazine (2.5 g, 16.5 mmol) was added rapidly to a solution of pentafluorophenyl-lithium [from pentafluorobenzene (5 g, 29.8 mmol) and butyl-lithium] in ether–hexane at $-78°$. After being stirred at $-78°$ for 2 h the mixture was allowed to warm to room temperature overnight and hydrolysed with dilute sulphuric acid. The organic layer was separated, washed with water (2×20 ml), dried ($MgSO_4$), and concentrated to *ca.* 50 ml. Cooling yielded crystals of *perfluoro-4,5-diphenylpyridazine* (2.0 g, 30%), m.p. 216—217° (from dichloromethane–ether) (Found: C, 43.2; F, 51.3; N, 6.2. $C_{16}F_{12}N_2$ requires C, 42.9; F, 50.9; N, 6.25%), ^{19}F δ (Me_2CO) 84.1 (F-3), 140.8 (F-2'), 150.9 (F-4'), and 162.3 p.p.m. (F-3'), m/e 448 (M^+, 100%) and 210 ($C_8F_6^+$, 35%), $\lambda_{max.}$ 268 nm (log ϵ 4.12), $\nu_{max.}$ (KBr) 1660, 1522, 1500vs, 1445, 1398, 1388, 1336w, 1309, 1129, 1098, 1043w, 1015, 1002, 997, 956, 807, 795, 782, 684w, and 672w cm^{-1}. The presence of perfluorotetraphenylpyridazine in the residual viscous oil was indicated by t.l.c.

Perfluoro-4,5-di-isopropyl-3,6-diphenylpyridazine (V).— Perfluoro-4,5-di-isopropylpyridazine (5.0 g, 11.1 mmol) in ether (70 ml) was added dropwise to pentafluorophenyl-lithium [from pentafluorobenzene (3.72 g, 22.1 mmol)] in ether (120 ml) and hexane (80 ml) at $-78°$. The mixture

was stirred at this temperature for 6 h and allowed to attain room temperature overnight. Dilute hydrochloric acid (100 ml) was then added, followed by ether (80 ml) to dissolve precipitated material. The organic layer was separated, dried ($MgSO_4$), and evaporated to *ca.* 10 ml. The yellow precipitate was filtered off and washed with cold dry ether to yield *perfluoro-4,5-di-isopropyl-3,6-diphenylpyridazine* (5.4 g, 65%), m.p. 139° [from chloroform-petroleum (b.p. 40—60°)] (Found: C, 35.0; N, 3.9; F, 61.2. $C_{22}F_{24}N_2$ requires C, 35.3; N, 3.7; F, 61.0%), ^{19}F δ (C_6F_6) 67.3 and 69.5 [$(CF_3)_2CF$], 136.0 and 139.8 (F-2'), 145.2 and 169.1 [$(CF_3)_2CF$], 148.4 and 151.2 (F-4'), and 161.1 p.p.m. (F-3'), m/e 748 (M^+, 12%), 729 [$(M - F)^+$, 10%], 720 [$(M - N_2)^+$, 20%], 360 ($C_6F_5 \cdot C \equiv C \cdot C_3F_7^+$, 100%), 358 ($C_6F_5 \cdot C \equiv C \cdot C_6F_5^+$, 10%), 291 ($C_{10}F_9^+$, 90%), and 241 ($C_9F_7^+$, 40%), $\lambda_{max.}$ (MeCN) 227 (log ϵ 3.99), 257 (4.06), and 381 nm (2.42).

Perfluoro-4,5-diethyl-3,6-diphenylpyridazine (IV).—Under conditions similar to those just described, reaction between pentafluorophenyl-lithium and perfluoro-4,5-diethylpyridazine yielded *perfluoro-4,5-diethyl-3,6-diphenylpyridazine* (60%), m.p. 144° (from carbon tetrachloride) (Found: C, 36.9; F, 58.65; N, 4.5. $C_{20}F_{20}N_2$ requires C, 37.1; F, 58.7; N, 4.2%), ^{19}F δ (C_6F_6) 77.0 (CF_3), 98.6 (CF_2), 138.3 (F-2'), 150.2 (F-4'), and 161.8 p.p.m. (F-3'), $J_{2,4}$ *ca.* 18.5 Hz, m/e 648 (M^+, 30%), 629 [$(M - F)^+$, 7%], 620 [$(M - N_2)^+$, 6%], 358 ($C_6F_5 \cdot C \equiv C \cdot C_6F_5$, 5%), 310 ($C_6F_5 \cdot C \equiv C \cdot C_2F_5^+$, 60%), and 241 ($C_9F_7^+$, 100%), $\lambda_{max.}$ 253.5 (log ϵ 3.82) and 373 nm (2.34).

Perfluoro-4,5-di-isopropyl-3,6-di-(4-pyridyl)pyridazine (VI).—Perfluoro-4,5-di-isopropylpyridazine (5.0 g, 11.1 mmol) in ether (70 ml) was added to tetrafluoro-4-pyridyl-lithium [23] [from 4-bromotetrafluoropyridine (4.3 g, 18.7 mmol)] in ether (100 ml) at $-78°$. After being stirred for 1 h the mixture was treated at $-78°$ with gaseous hydrogen chloride. It was then allowed to warm to room temperature, water (100 ml) was added, and the organic layer was separated and dried ($MgSO_4$). Removal of solvent gave a semi-solid residue which was recrystallised from ethanol to give *perfluoro-4,5-di-isopropyl-3,6-di-(4-pyridyl)-pyridazine* (3.4 g, 50%), m.p. 120—121° (Found: C, 33.3; F, 58.0; N, 8.2. $C_{20}F_{22}N_4$ requires C, 33.6; F, 58.55; N, 7.85%), ^{19}F δ 67.3 and 69.7 [$(CF_3)_2CF$], 88.0 (F-2'), 137.0 and 141.5 (F-3'), and 143.3 and 168.4 [$(CF_3)_2CF$], m/e 714 (M^+, 35%), 695 [$(M - F)^+$, 15%], 686 [$(M - N_2)^+$, 15%], 343 ($C_5F_4N \cdot C \equiv C \cdot C_3F_7^+$, 100%), 274 ($C_9F_8N^+$, 50%), and 224 ($C_8F_6N^+$, 40%).

Pyrolysis of Perfluorotetraphenylpyridazine (I).—Perfluorotetraphenylpyridazine (140 mg), was sublimed from a heated tube (280°) *in vacuo* (0.002 mmHg) through a silica tube loosely packed with silica wool heated to $725 \pm 15°$ for *ca.* 20 cm. Crystals condensed in two zones in a cool extension to the furnace to give unchanged perfluorotetraphenylpyridazine (44 mg) and perfluorodiphenylacetylene (84 mg, 90%) (70% conversion), m.p. 120—122.5 (from ethanol) (lit.,[25] 122—123°; lit.,[26] 123—123.5°), identified by its spectroscopic properties.

Pyrolysis of Perfluoro-4,5-di-isopropyl-3,6-diphenylpyridazine (V).—The pyridazine (V) (250 mg) at 150° was transferred under vacuum conditions (0.01 mmHg) through a silica tube (volume *ca.* 30 cm³) lined and loosely packed with platinum heated to 680°, and the product was collected

[23] E. Kinsella and A. G. Massey, *Chem. and Ind.*, 1971, 1017.
[24] R. D. Chambers, F. G. Drakesmith, and W. K. R. Musgrave, *J. Chem. Soc.*, 1965, 5045.

[25] R. Filler and E. W. Heffern, *J. Org. Chem.*, 1967, **32**, 3249.
[26] J. M. Birchall, F. L. Bowden, R. N. Haszeldine, and A. B. P. Lever, *J. Chem. Soc.* (A), 1967, **747**.

in a liquid-air trap. Vacuum transfer yielded *perfluoro-3-methyl-1-phenylbut-1-yne* (202 mg, 84%) (Found: C, 36·95; F, 62·85. $C_{11}F_{12}$ requires C, 36·65; F, 63·35%), ^{19}F δ 76·2 $[(CF_3)_2CF]$, 133·5 (F-2'), 147·3 (F-4'), 160·8 (F-3'), and 167·2 p.p.m. $[(CF_3)_2CF]$, *m/e* 360 (M^+, 40%), 341 $[(M - F)^+, 25\%]$, 291 $[(M - CF_3)^+, 60\%]$, and 241 $(C_9F_7^+, 100\%)$, $v_{max.}$ (C≡C str.) *ca.* 2255 cm^{-1}.

Pyrolysis of Perfluoro-4,5-diethyl-3,6-diphenylpyridazine (IV).—Under similar conditions, the pyridazine (IV) (870 mg), at 720° yielded *perfluoro-1-phenylbut-1-yne* (736 mg, 88%) (Found: C, 38·5; F, 60·9. $C_{10}F_{10}$ requires C, 38·7; F, 61·3%), ^{19}F δ 85·8 (CF$_3$), 103·6 (CF$_2$), 134·4 (F-2'), 148·0 (F-4'), and 161·6 (F-3'), *m/e* 310 (M^+, 40%), 291 $(C_{10}F_9^+$, 12%), 241 $(C_9F_7^+, 100\%)$, and 141 $(C_7F_3^+, 8\%)$, $v_{max.}$ (C≡C str.) *ca.* 2260 cm^{-1}.

Pyrolysis of Perfluoro-4,5-di-isopropyl-3,6-di-(4-pyridyl)-pyridazine (VI).—Similarly, the pyridazine (VI) (684 mg) at 700° yielded *perfluoro-3-methyl-1-(4-pyridyl)but-1-yne* (540 mg, 82%) (Found: C, 35·2; F, 60·4; N, 4·3. $C_{10}F_{11}N$ requires C, 35·0; F, 60·9; N, 4·1%), ^{19}F δ 79·4 $[(CF_3)_2CF]$, 91·8 (F-2'), 139·0 (F-3'), and 172·0 p.p.m. $[(CF_3)_2CF]$, *m/e* 343 (M^+, 90%), 324 $[(M - F)^+, 30\%]$, 274 $(C_9F_8N^+, 45\%)$, and 224 $(C_8F_6N^+, 100\%)$, $v_{max.}$ (C≡C str.) *ca.* 2260 cm^{-1}.

Pyrolysis of Tetrachloropyridazine.—In a typical experiment, tetrachloropyridazine (4·2 g), heated to 150°, was passed through a silica tube loosely packed with silica wool at 680 ± 10° in a stream of dry nitrogen (contact time *ca.* 45 s). The product was collected in two main fractions; a solid (A) (0·45 g) which was deposited on a cool extension from the furnace, and the remainder (B) in a liquid air trap. After removal of elemental chlorine, fraction (B) (2·1 g) was shown by g.l.c., mass spectrometry, and i.r.

^{27} H. Mommaerts, *Bull. class. sci. Acad. roy. Belg.*, 1941, **27**, 549 (*Chem. Abs.*, 1944, **38**, 3621).

^{28} R. D. Chambers, J. Hutchinson, and W. K. R. Musgrave, *J. Chem. Soc.*, 1964, 3573.

spectroscopy to contain hexachlorobutadiene (1·5 g, 30%), tetrachloroethylene (0·3 g, 10%), and a mixture of dichlorofumaronitrile and dichloromaleonitrile (0·3 g, 10%);^{27} pure samples were obtained by preparative scale g.l.c. Analysis of sublimed fractions of the solid material (A) by similar techniques indicated the presence of tetrachloropyridazine (0·25 g), pentachloropyridine ^{28} (15 mg, *ca.* 0·3%), hexachlorobenzene (125 mg, *ca.* 5%), pentachlorobenzonitrile ^{29} (27 mg, *ca.* 1%), tetrachloro-*o*-phthalonitrile ^{30} (10 mg, *ca.* 0·4%), and octachlorostyrene ^{31} (17 mg, *ca.* 0·5%). A trace of octachloroacenaphthalene,^{32} deposited immediately outside the furnace exit, was also obtained (5 mg, *ca.* 0·2%).

Pyrolysis of Hexachlorocinnoline.—Hexachlorocinnoline (304 mg) was sublimed under vacuum conditions through a silica tube loosely packed with silica wool heated to 770 ± 10°. Crystals condensed in two zones in a cool extension to the furnace to give (i) an unidentified red substance (14 mg, nearer furnace), and (ii) *hexachlorophenylacetylene* (103 mg, 37%), m.p. 137—138·5° (from di-isopropyl ether) (Found: C, 30·8%; *M*, 306. C_8Cl_6 requires C, 31·1%; *M*, 306), $\lambda_{max.}$ (cyclohexane), 228, 233, 255, and 275 nm, $v_{max.}$ (C≡C str.) 2222 cm^{-1}.

Pyrolysis of Hexachlorophthalazine.—The pyrolysis of hexachlorophthalazine (500 mg) under vacuum conditions (silica tube) at 775° yielded pale yellow crystals of tetrachlorophthalonitrile ^{30} (360 mg, 92%), m.p. 254—257° (from acetonitrile) (lit.,^{30} 243·6—244·3°) (Found: C, 35·25%; *M*, 264. Calc. for $C_8Cl_4N_2$: C, 35·1%; *M*, 264), identified by spectroscopic properties.

^{29} J. M. Birchall, R. N. Haszeldine, and M. E. Jones, *J. Chem. Soc.* (C), 1971, 1343.

^{30} B.P. 982,892 (*Chem. Abs.*, 1965, **62**, 16,150).

^{31} J. N. Seiber, *J. Org. Chem.*, 1971, **36**, 2000.

^{32} W. Mack, *Tetrahedron*, 1966, **25**, 2875.