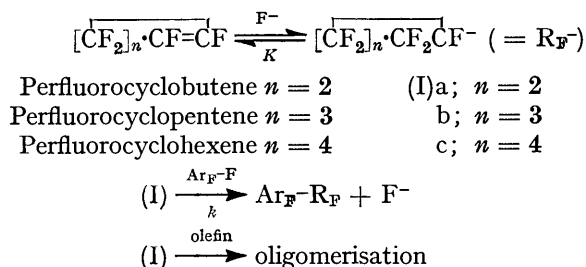


Reactions Involving Fluoride Ion. Part VIII.¹ Syntheses from Perfluorocycloalkenes

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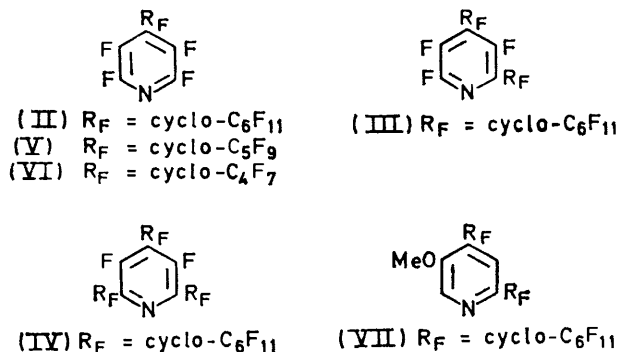
Perfluorocyclo-hexene, -pentene, and to a lesser extent, -butene react with pentafluoropyridine in the presence of caesium fluoride to give perfluorocycloalkylpyridines. Di- and tri-substituted pyridines are obtained only from perfluorocyclohexene, and perfluorocycloalkyl derivatives are isolated only from perfluorocyclohexene on reaction of these cyclic olefins with tetrafluoropyridazine. Fluoride ion induces dimerisation of perfluorocyclo-pentene and -hexene whereas a trimer of perfluorocyclobutene is isolated; the structures of these products are established.

EXTENDING the methods which we developed earlier,^{1,2} we now describe some reactions of perfluorocycloalkyl-anions, generated from perfluorocycloalkenes with fluoride ion.



Perfluorocycloalkyl-pyridines and -pyridazines were obtained by reactions of these perfluorocycloalkyl anions (Ia—c) with pentafluoropyridine and tetrafluoropyridazine. Oligomerisation of the olefins also occurred but this competing process (see below) was suppressed by performing the reactions at atmospheric pressure.

Perfluorocyclohexene and pentafluoropyridine reacted together slowly at 80° in tetrahydrothiophen dioxide, in the presence of caesium fluoride, to give perfluoro-4-cyclohexylpyridine (II) (95%) together with traces of the dicycloalkyl derivative (III). Significant amounts of product (III) as well as the tricycloalkyl derivative (IV)



were obtained, however, by carrying out the reactions using sealed tubes under forcing conditions (165—170°).

¹ Part VII, R. D. Chambers and M. Y. Gribble, *J.C.S. Perkin I*, 1973, 1411.

² R. D. Chambers and M. Y. Gribble, *J.C.S. Perkin I*, 1973, 1405, and references therein.

³ M. J. Roura Fraticelli, Ph.D. Thesis, Cornell University, 1965 (*Diss. Abs.*, 1965, **26**, 3045).

Perfluorocyclopentene reacted slowly with pentafluoropyridine at 80° to give the monosubstituted pyridine (V) (80% yield, 45% conversion) but reactions in sealed tubes, which were necessary at higher temperatures, led to dimerisation of perfluorocyclopentene in preference to further substitution in the pyridine (V). It was even more difficult to avoid oligomerisation³ in reactions with perfluorocyclobutene; this was diluted with nitrogen at atmospheric pressure but, while oligomerisation was suppressed under these conditions, only a low conversion into the pyridine (VI) was obtained.

Perfluorocyclobutene is the least efficient of the three cyclic olefins in the perfluorocycloalkylation, but this is not a reflection of the relative reactivities of the intermediate anions (Ia—c). The observed rate of perfluorocycloalkylation is a product of an equilibrium constant *K*, for reaction between fluoride ion and the olefin, and a rate constant *k* for reaction of the anion (Ia) with the perfluoroaromatic compound.² A necessarily low concentration of perfluorocyclobutene, to avoid oligomerisation, leads to a correspondingly low concentration of anion (Ia) which in turn results in slow conversion into the substituted product (VI); the rate constants, *k*, for substitution by the anions (Ia—c) could be similar.

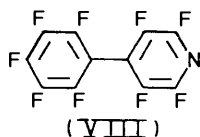
The three cyclic olefins are much less efficient in polyfluoroalkylation than hexafluoropropene; reaction of this olefin with pentafluoropyridine gives both perfluoro-2,4,5- and -2,4,6-tri-isopropylpyridines, these being the products of kinetic and thermodynamic control, respectively.^{4,5} However, under the more vigorous conditions required to give trisubstitution from perfluorocyclohexene, only the product of thermodynamic control (IV) was obtained. Nevertheless, that nucleophilic attack on the dicyclohexyl derivative (III) may occur preferentially at the 5-position is illustrated by the reaction of the derivative (III) with methoxide ion, when the 5-methoxypyridine (VII) was obtained exclusively. This is analogous to the orientation of attack by methoxide in perfluoro-2,4-diethyl- and -di-isopropyl-pyridines.²

The structures of the cycloalkyl compounds (II), (V), and (VI) may be predicted from the fact that monosubstitution in pentafluoropyridine with a variety

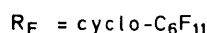
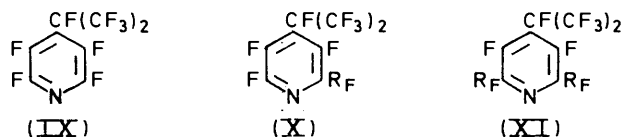
⁴ R. D. Chambers, R. P. Corbally, and W. K. R. Musgrave, *J.C.S. Perkin I*, 1972, 1281.

⁵ R. D. Chambers, R. P. Corbally, M. Y. Gribble, and W. K. R. Musgrave, *Chem. Comm.*, 1971, 1345.

of nucleophiles,^{6,7} including perfluoroalkylanions,² occurs exclusively at the 4-position. Nevertheless, the ¹⁹F n.m.r. spectra confirm these assignments; in each case the spectra are complex, and have not been fully analysed, but the characteristic resonances arising from the 2- and 6-fluorine atoms in the pyridine ring are easily distinguishable at lower field.⁸ A single band corresponding to two fluorine atoms is observed in each case, indicating the symmetrical structures (II), (V), and (VI). Furthermore, defluorination⁹ of the cyclohexyl derivative (II) over iron gave the known perfluoro-4-phenylpyridine¹⁰ (VIII).

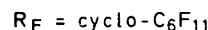


The structure of the dicyclohexyl derivative (III) is evident from the presence of a low-field resonance corresponding to one fluorine atom, *i.e.* at the 6-position, and the structure of the ether (VII), formed by attack of methoxide ion on the derivative (III), followed from a similar observation. The very complex spectrum obtained from the tricyclohexyl derivative (IV) could not be analysed, but the structure was deduced from the absence of any low-field resonance attributable to a fluorine atom in the 6-position of the pyridine ring. Reaction of perfluoro-4-isopropylpyridine (IX) with perfluorocyclohexene gave the derivatives (X) and (XI), whose structures were assigned on a similar basis.



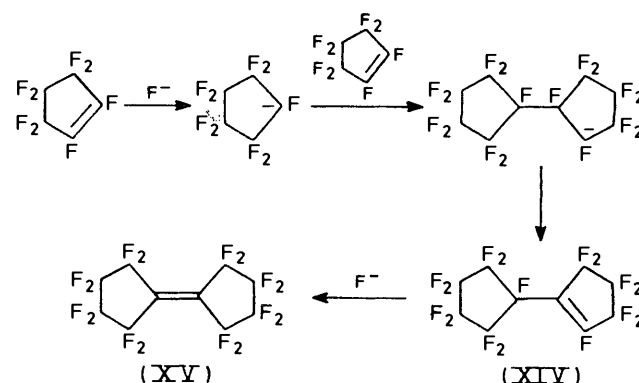
Reaction of perfluorocyclohexene with tetrafluoropyridazine gave a high yield of a product which contained mainly perfluoro-4-cyclohexylpyridazine (XII), together with traces of perfluoro-3,5-dicyclohexylpyridazine (XIII). Reactions between tetrafluoropyridazine and either perfluorocyclopentene or -butene were unsuccessful under a variety of conditions. Perfluorocyclopentene reacts with pentafluoropyridine (see before) and, since tetrafluoropyridazine is more reactive than

pentafluoropyridine to nucleophilic attack,^{11,12} it would be expected that the former would react more



efficiently than the latter with perfluorocyclopentene. This result is not yet understood.

The analogy between the role of fluoride ion, in reactions with unsaturated fluorocarbons, and the proton, in reactions with unsaturated hydrocarbons, has been stressed previously.^{13,14} Oligomers are formed in fluoride-ion induced reactions of tetrafluoroethylene,^{15,16} hexafluoropropene,^{3,17-20} octafluoroisobutene,^{21,22} and hexafluorocyclobutene^{3,23} and we have now found that,



SCHEME 1

using reactions in sealed tubes, dimerisation of perfluorocyclopentene and perfluorocyclohexene will occur in the presence of caesium fluoride. Heating perfluorocyclopentene with anhydrous caesium fluoride and tetrahydrothiophen dioxide in a sealed tube at 125° gave the dimer (XV) in 86% yield and its mechanism of formation is shown in Scheme 1. The olefin (XIV), which is probably the initial product, is not isolated but is converted into the symmetrical olefin (XV) by a fluoride-ion induced allylic rearrangement. The structure of dimer (XV) follows from the ¹⁹F n.m.r. spectrum,

¹⁴ R. D. Chambers, R. A. Storey, and W. K. R. Musgrave, *Chem. Comm.*, 1966, 384.

¹⁵ D. P. Graham, *J. Org. Chem.*, 1966, **31**, 955.

¹⁶ H. C. Fielding and A. J. Rudge, *B.P.* 1,082,127/1967.

¹⁷ W. J. Brehm, K. G. Brenner, H. S. Eleuterio, and R. W. Meschke, *U.S.P.* 2,918,501/1959.

¹⁸ R. D. Dresdner, F. N. Tlumac, and J. A. Young, *J. Org. Chem.*, 1965, **30**, 3524.

¹⁹ R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, and R. A. Storey, *J. Chem. Soc. (C)*, 1963, 2221.

²⁰ W. Brunskill, W. T. Flowers, R. Gregory, and R. N. Haszeldine, *Chem. Comm.*, 1970, 1444.

²¹ D. P. Graham and W. B. McCormack, *J. Org. Chem.*, 1966, **31**, 958.

²² D. L. Miller, *U.S.P.* 3,389,187/1968.

²³ R. L. Pruett, C. T. Bahner, and H. A. Smith, *J. Amer. Chem. Soc.*, 1952, **74**, 1638.

⁶ R. D. Chambers, J. Hutchinson, and W. K. R. Musgrave, *J. Chem. Soc.*, 1964, 3736.

⁷ R. E. Banks, J. E. Burgess, W. M. Cheng, and R. N. Haszeldine, *J. Chem. Soc.*, 1965, 575.

⁸ R. D. Chambers, J. Hutchinson, and W. K. R. Musgrave, *J. Chem. Soc. (C)*, 1966, 220.

⁹ B. Gething, C. R. Patrick, M. Stacey, and J. C. Tatlow, *Nature*, 1959, **183**, 588.

¹⁰ R. D. Chambers, J. Hutchinson, and W. K. R. Musgrave, *J. Chem. Soc.*, 1965, 5040.

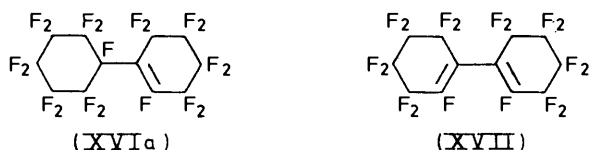
¹¹ R. D. Chambers, J. A. H. MacBride, and W. K. R. Musgrave, *J. Chem. Soc. (C)*, 1963, 2116.

¹² J. S. Waterhouse, unpublished results.

¹³ W. T. Miller, J. H. Fried, and H. Goldwhite, *J. Amer. Chem. Soc.*, 1960, **82**, 3091.

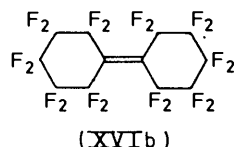
which shows two resonances of equal intensity and at a region corresponding to difluoromethylene groups in a cyclic system.

Perfluorocyclohexene gave the unsymmetrical dimer (XVIa) together with the product of defluorination (XVII). The structure of dimer (XVIa) followed mainly from the identification of the characteristic high-



field resonance (181.9 p.p.m., 1F) in the ^{19}F n.m.r. spectrum indicating the presence of only one tertiary fluorine, *i.e.* that at the ring junction; only structure (XVIa) is consistent with this signal. No tertiary fluorine resonance occurred in the ^{19}F n.m.r. spectrum of the product (XVII), thus eliminating structures with both double bonds in one ring as well as structures where the double bonds are not conjugated; four resonances were observed and the relative intensities are only consistent with structure (XVII).

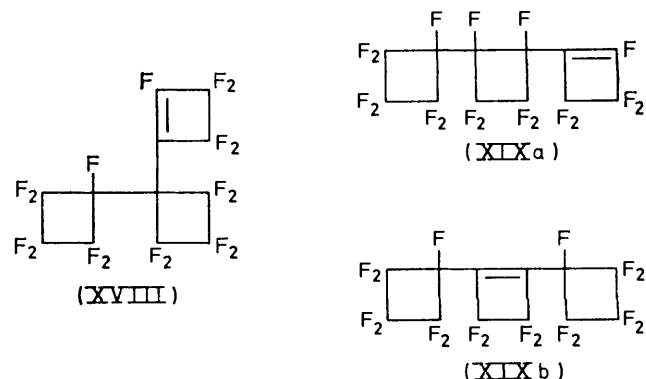
The diene (XVII) has been obtained previously by coupling of 1-bromononafluorocyclohexene²⁴ by use of copper bronze and, more recently, it has been shown to be a component of the complex mixture obtained from irradiation of perfluorocyclohexene.²⁵ Also, dimer (XVIa) has been prepared, together with compound (XVIb), by mild fluorination of the diene (XVII) with cobalt trifluoride.²⁵ Since only dimer (XVIa) is



isolated under forcing conditions, we conclude that it is the more stable isomer.

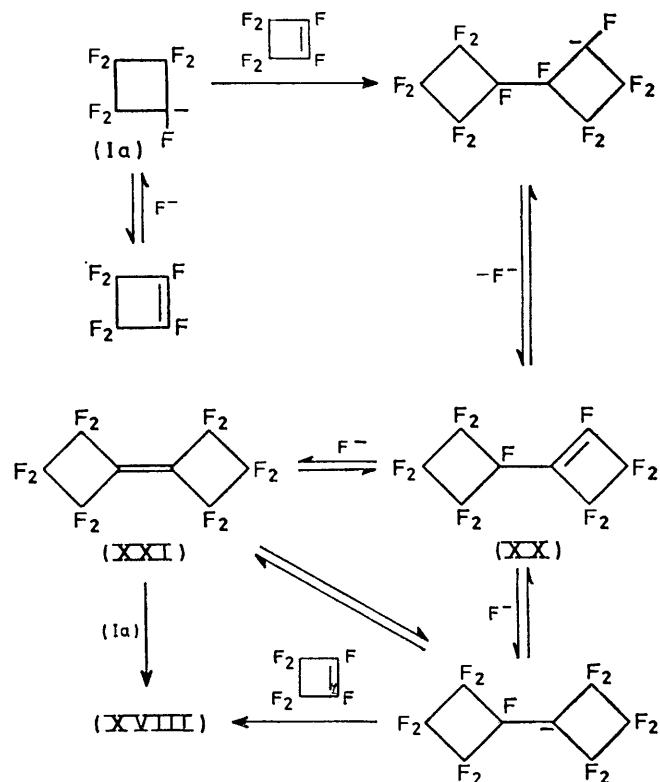
The formation of dimers and a trimer from perfluorocyclobutene with fluoride ion has been reported previously.^{3,23} We have assigned the structure (XVIII) to the trimer, in contrast to the structures (XIXa)²³ and (XIXb)³ which have been proposed previously. The ^{19}F n.m.r. spectrum is complex but at high field (173.00 p.p.m., relative to CFCl_3) there is a signal, integrating for one fluorine, which is very characteristic of a single fluorine atom attached to a saturated carbon; while at low field (91.3 p.p.m.) there is a clearly defined signal, also due to one fluorine, which is only consistent with fluorine attached to a vinylic carbon atom. Only structure (XVIII) is consistent with these n.m.r. data. Also, electron-induced photoelectron spectroscopic measurement²⁶ of the carbon 1s binding energies and their integrations are consistent with the presence of eight saturated carbon atoms each with two attached

fluorine atoms, one saturated carbon with one attached fluorine, one saturated carbon with no attached fluorine,



one vinylic carbon with one attached fluorine, and one vinylic carbon with no attached fluorine.

The formation of trimer (XVIII) could occur by two alternative routes, shown in Scheme 2, which we cannot distinguish on the basis of present results. Dimers (XX) and (XXI) have been isolated by other workers^{3,23} but under the conditions which we have employed only trimer (XVIII) was isolated, with the dimers present in only trace quantities.



SCHEME 2

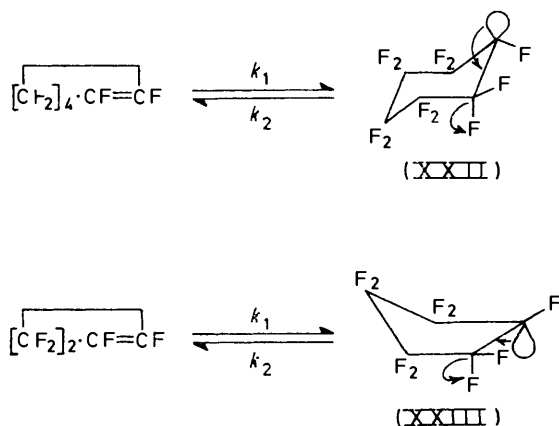
The results presented here show that fluoride-ion initiated reactions of perfluorocycloalkenes occur much

²⁴ G. Camaggi, S. F. Campbell, D. R. A. Perry, R. Stephens, and J. C. Tatlow, *Tetrahedron*, 1966, **22**, 1755.

²⁵ G. Camaggi and F. Gozzo, *J. Chem. Soc. (C)*, 1971, 925.

²⁶ Unpublished data.

less readily than analogous reactions of hexafluoropropene and the most likely explanation for this difference lies in a much reduced equilibrium constant for the formation of the cyclic anions (Ia—c). Terminal difluoromethylene groups are known to be very susceptible to nucleophilic attack²⁷ and, therefore, the forward reaction k_1 , addition of fluoride ion, is probably less efficient in the cyclic series. Also, the cyclic anions have an enforced stereochemistry which provides for the energetically favourable coplanar *anti*- or *syn*-elimination²⁸ of fluoride ion, as illustrated for (XXII) and (XXIII).



This means that the back reaction, k_2 , loss of fluoride ion, is almost certainly more efficient in the cyclic series, leading to a lower equilibrium concentration of carbanions.

EXPERIMENTAL

¹⁹F and ¹H N.m.r. spectra were measured at 40° using a Varian A56/60D spectrometer, with trichlorofluoromethane or tetramethylsilane as external reference. Upfield shifts are quoted as positive.

Fluoride-ion Induced Reactions of Pentafluoropyridine.—

(a) *With decafluorocyclohexene.* (i) At atmospheric pressure. The apparatus is as described.² A dry flask containing caesium fluoride (3.0 g, 19.7 mmol) and tetrahydrothiophen dioxide (30 ml) was evacuated and then heated to *ca.* 80°. The system was then equilibrated to atmospheric pressure with dry nitrogen, after which pentafluoropyridine (3.0 g, 17.8 mmol) and perfluorocyclohexene (4.65 g, 18.0 mmol) were added through a serum cap. The mixture was stirred vigorously, and after 42 h the volatile material (6.5 g) was transferred from the flask, under high vacuum, to a flask cooled in liquid air. The liquid product was analysed by g.l.c. (gas density balance detector) and the yield of compound (II) was calculated (95% based on a 55% conversion of pentafluoropyridine). Samples were separated using preparative-scale g.l.c. instrument (diisodecyl phthalate on Celite; 150°). Recovered starting compounds were identified by comparison of their i.r. spectra with those of authentic samples and *perfluoro-4-cyclohexylpyridine* (II) was obtained as a crystalline solid, m.p. 33.5—34.5° (Found: C, 30.3; F, 66.5%; M^+ , 431. $C_{11}F_{15}N$ requires C, 30.6; F, 66.1%; M , 431); λ_{max} (cyclohexane) 284 nm (ϵ 4758); i.r. λ_{max} 6.81, 7.78, 7.84,

7.92, 8.03, 8.19, 8.40, 8.49, 10.23, 10.33, 10.54, and 14.69 μ m; δ_F 87.2 (2,6-F) and 180.8 (—CF<) and numerous signals at 113—145 p.p.m. (unassigned); the overall integration was consistent with structure (II).

Crystals (0.2 g) recovered from the neck of the reaction flask were identified as *perfluoro-2,4-dicyclohexylpyridine* (III), m.p. 78—79° (Found: C, 29.3; F, 68.9%; M^+ , 693. $C_{17}F_{25}N$ requires C, 29.4; F, 68.5%; M , 693); λ_{max} (cyclohexane) 279 nm (ϵ 5381); i.r. λ_{max} 8.01, 8.13, 8.41, 9.68, 9.79, and 10.3 μ m; δ_F 81.3 (2F, 6-F) and 180.4 (2F, —CF<) and complex overlapping signals at 106—146 p.p.m. (22F, unassigned). The residual involatile material from the flask was poured into water (400 ml), acidified (dilute hydrochloric acid), and extracted with ether (4 \times 25 ml). The combined extracts were washed with water (2 \times 10 ml), dried (MgSO₄), and evaporated, and the residual orange oil (0.55 g) was analysed by g.l.c. and shown not to contain any tractable products.

(ii) In a sealed tube. A mixture of caesium fluoride (5.0 g, 32.8 mmol), tetrahydrothiophen dioxide (60 ml), pentafluoropyridine (V) (3.0 g, 17.8 mmol), and perfluorocyclohexene (10.0 g, 38.2 mmol) was heated in a nickel tube for 75 h at 165°. After cooling, the volatile products (2.8 g) were transferred under vacuum to a cold trap, and shown by g.l.c. to consist mainly of the monosubstituted pyridine (II) (1.8 g) and the dimer (XVII) (0.75 g). Samples were separated by preparative scale g.l.c. and identified by comparison of their i.r. spectra with those of authentic samples. The involatile product mixture was poured into water (400 ml) and extracted with ether (3 \times 25 ml). On washing the combined extracts with ether a small quantity of crystals was precipitated, and these were sublimed at 110° under vacuum to give *perfluoro-2,4,6-tricyclohexylpyridine* (IV), (0.2 g), m.p. 112—114° (Found: C, 29.2; F, 70.1%; M^+ , 955. $C_{23}F_{35}N$ requires C, 28.9; F, 69.6%; M , 955), λ_{max} (cyclohexane) 273 nm (ϵ 4618); i.r. λ_{max} 7.92, 8.00, 8.18, 8.41, 9.67, 9.76, 10.35, 10.76, 11.12, and 15.71 μ m; δ_F 178.3 (1F, —CF<), 182.5 (2F, —CF<), and 100.4 [2F, 3,5-F (*cf.* the observed chemical shift in perfluoro-2,4,6-trialkylpyridines²⁹)] and numerous signals at 115—150 p.p.m. (30F, unassigned). The ether extracts were dried (MgSO₄) and evaporated to give a dark brown viscous liquid, which was sublimed under vacuum up to 120°. Recrystallisation of the sublimate from petroleum (b.p. 40—60°) gave the disubstituted pyridine (III) (1.2 g).

(b) *With octafluorocyclopentene.* (i) At atmospheric pressure. A mixture of caesium fluoride (3.0 g, 19.7 mmol), tetrahydrothiophen dioxide (30 ml), pentafluoropyridine (4.25 g, 25.1 mmol), and perfluorocyclopentene (13.5 g, 63.7 mmol) was stirred vigorously for 144 h at *ca.* 80°. The volatile material (11.7 g) was transferred from the flask, under high vacuum, to a cold trap and then separated by fractional distillation into a gaseous component (1.0 g), identified spectroscopically as perfluorocyclopentene, and a liquid (10.7 g). The latter was analysed by g.l.c. and the yield of (V) was calculated (80% based on a 45% conversion of pentafluoropyridine). Compound (XV) and pentafluoropyridine, separated by distillation, were identified by comparison of their i.r. spectra with those of authentic samples, and *perfluoro-4-cyclopentylpyridine* (V) was obtained as needles, m.p. 48.5—49.5° (Found: C, 31.3; F,

²⁸ D. V. Banthorpe, 'Elimination Reactions,' Elsevier, Amsterdam, 1963.

²⁹ R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, L. H. Sutcliffe, and G. J. T. Tiddy, *Tetrahedron*, 1970, **26**, 71.

²⁷ R. D. Chambers and R. H. Mobbs, *Adv. Fluorine Chem.*, 1965, **4**, 50 and references therein.

65.1%; M^+ , 381. $C_{10}F_{13}N$ requires C, 31.5; F, 64.8%; M , 381; λ_{\max} (cyclohexane) 284 nm (ϵ 4451); i.r. λ_{\max} 6.73, 7.63, 8.22, 10.47, and 12.98 μm ; δ_F 87.0 (2,6-F) and 167.9 ($-\text{CF}<$) and numerous signals at 115—135 p.p.m. (unassigned). The residual involatile material was treated in the usual manner and gave a brown oil (1.0 g) which did not contain any identifiable or tractable products.

(ii) In a sealed tube. Similar reactions between perfluorocyclopentene and pentafluoropyridine in sealed tubes at temperatures up to *ca.* 175° for up to 48 h resulted in increased formation of the dimer (XV), but neither higher conversion of pentafluoropyridine into the monosubstituted product (V) nor the formation of di- or tri-cyclopentyl derivatives.

(c) *With hexafluorocyclobutene.* (i) At atmospheric pressure. A mixture of caesium fluoride (3.9 g, 19.7 mmol), tetrahydrothiophen dioxide (30 ml), and pentafluoropyridine (2.9 g, 17.1 mmol), under an atmosphere of perfluorocyclobutene (7.0 g, 43.2 mmol) diluted with dry nitrogen, was stirred vigorously at *ca.* 25° for 360 h. The volatile material (4.35 g) was removed from the flask, under high vacuum, to a cold trap; fractional distillation of this material gave a gaseous component (0.5 g), identified spectroscopically as perfluorocyclobutene, and a liquid (3.85 g). The liquid was analysed by g.l.c. and the yield of (VI) was calculated [35% based on a 10% conversion of pentafluoropyridine]. Samples were separated by preparative scale g.l.c.; pentafluoropyridine and compound (XXIII) were identified by comparison of their i.r. spectra with those of authentic samples and *perfluoro-4-cyclobutylpyridine* (VI) was obtained as a liquid, b.p. 154.5° at 760 mmHg (Found: C, 32.9; F, 63.4%; M^+ , 331. $C_9F_{11}N$ requires C, 32.6; F, 63.1; M , 331); λ_{\max} (cyclohexane) 284 nm (ϵ 3718); i.r. λ_{\max} 6.71, 7.64, 8.16, 8.33, 10.75, and 12.65 μm ; δ_F 87.0 (2,6-F), 137.5 (3,5-F), and 167.1 ($-\text{CF}<$) and numerous signals at 125—136 p.p.m. (unassigned). The residual involatile material was worked up in the usual manner and gave a brown oil (1.25 g) which contained no identifiable products.

Similar reactions using an atmosphere of undiluted hexafluorocyclobutene resulted in a marginal increase in its trimerisation, but greater conversion of pentafluoropyridine into the monosubstituted product (VI) was not achieved.

(ii) In sealed tubes. The major product from similar reactions in sealed tubes at temperatures up to *ca.* 180° was the trimer (XVIII); unchanged pentafluoropyridine and small amounts of the product (VI) were also obtained.

Fluoride-ion Induced Reaction of Perfluoro-4-isopropylpyridine (IX) with Decafluorocyclohexene.—A mixture of caesium fluoride (5.0 g, 32.9 mmol), tetrahydrothiophen dioxide (60 ml), perfluorocyclohexene (6.5 g, 24.8 mmol), and the pyridine (IX) (3.0 g, 9.4 mmol) was heated in a nickel tube for 64 h at *ca.* 165°. The volatile material (5.0 g), which was transferred under vacuum to a cold trap, was separated by vacuum distillation into a liquid (3.8 g) and a solid (1.2 g). The solid was recrystallised [from petroleum (b.p. 40—60°)] and shown to be *perfluoro-2,6-dicyclohexyl-4-isopropylpyridine* (XI), m.p. 120—122° (Found: C, 28.4; F, 69.8%; M^+ , 843. $C_{20}F_{31}N$ requires C, 28.5; F, 69.9%; M , 843); λ_{\max} (cyclohexane) 271 nm (ϵ 4080); i.r. λ_{\max} 7.58, 7.71, 7.95, 8.18, 8.31, 9.77, 9.92, 10.16, and 10.34 μm ; δ_F 74.5 (CF_2), 103.2 (3,5-F), and 182.1 ($-\text{CF}<$) and numerous signals at 111—147 p.p.m. (unassigned).

Analysis of the distillate by g.l.c. gave the yield of (X) [10% based on a 90% conversion of (IX)]. Samples were

separated using preparative scale g.l.c. and compounds (IX), (XVIa), and (XVII) were identified by comparison of their i.r. spectra with those of authentic samples. *Perfluoro-2-cyclohexyl-4-isopropylpyridine* (X) was obtained as a liquid, b.p. 203° at 760 mmHg (Found: C, 28.6; F, 69.0%; M^+ , 581. $C_{14}F_{21}N$ requires C, 28.9; F, 68.7%; M , 581); λ_{\max} (cyclohexane) 274 nm (ϵ 5437); i.r. λ_{\max} 6.78, 7.75, 8.06, 8.84, and 10.38 μm ; δ_F 71.7 (CF_2), 81.8 (6-F), and 179.8 and 182.5 ($-\text{CF}<$) and several signals at 112—147 p.p.m. (unassigned). The residual involatile material was worked up in the usual manner to give a dark, viscous residue from which, at 90—125° and 0.01 mmHg, a yellow solid was sublimed. Recrystallisation of this solid [petroleum (b.p. 40—60°)] gave the disubstituted product (XI) (0.5 g, total yield 22%), identified by i.r. spectroscopy.

Reaction of Perfluoro-4-cyclohexylpyridine (II) with Sodium Methoxide.—To a stirred solution of the pyridine (II) (0.45 g, 1.04 mmol) in dry methanol (40 ml) heated under reflux under dry nitrogen, was added a solution of sodium (0.027 g, 1.17 mmol) in dry methanol (10 ml) over 25 min. The solution was heated under reflux for a further 18 h, and the mixture was then allowed to cool and poured into water (300 ml). The aqueous mixture was extracted twice with methylene chloride, and the combined extracts were dried (MgSO_4). Evaporation left a solid which was sublimed (25—30° at 0.02 mmHg) to give *3,5,6-trifluoro-2-methoxy-4-undecafluorocyclohexylpyridine* (0.4 g, 87%), m.p. 45—46° (Found: C, 32.2; H, 0.62; F, 60.2%; M^+ , 443. $C_{12}H_3F_{14}NO$ requires C, 32.5; H, 0.67; F, 60.0%; M , 443); λ_{\max} (cyclohexane) 303 nm (ϵ 5498); i.r. λ_{\max} 6.71, 6.95, 7.12, 7.59, 7.8—8.1, 8.17, 8.48, 9.59, 9.80, 10.3—10.5, 10.9, 12.82, 13.42, and 15.69 μm ; δ_F 90.7 (6-F) and numerous complex signals at 115—147 p.p.m. (unassigned); δ_H 4.03 p.p.m. downfield from Me_4Si .

Reaction of Perfluoro-2,4-dicyclohexylpyridine (III) with Sodium Methoxide.—A solution of sodium (0.033 g, 1.4 mmol) in methanol (8 ml) was added to a stirred solution of the pyridine (III) (0.95 g, 1.37 mmol) in methanol (20 ml) during 30 min at *ca.* 20°. The mixture was then heated to *ca.* 80° and stirred for a further 20 h, cooled, poured into water (100 ml), acidified (dilute hydrochloric acid), and extracted with methylene chloride (3 \times 20 ml). The combined extracts were dried (MgSO_4) and evaporated to leave a pale yellow liquid (0.9 g). G.l.c. showed a single component, *3,6-difluoro-5-methoxy-2,4-bisundecafluorocyclohexylpyridine* (VII) (0.9 g, 90%), b.p. >260° (Found: C, 30.7; H, 0.52; F, 64.6%; M^+ , 705. $C_{13}H_3F_{24}NO$ requires C, 30.6; H, 0.42; F, 64.7%; M , 705); λ_{\max} (cyclohexane) 288 nm (ϵ 4804); i.r. λ_{\max} 7.90, 8.03, 8.16, 8.42, 9.71, and 10.37 μm ; δ_F 79.3 (6-F), and 180.7 and 185.3 ($-\text{CF}<$) and numerous complex signals at 111—150 p.p.m. (unassigned); δ_H 4.05 p.p.m. downfield from Me_4Si .

Defluorination of Perfluoro-4-cyclohexylpyridine (II).—Perfluoro-4-cyclohexylpyridine (II) (0.5 g, 1.16 mmol) was passed as vapour in a stream of nitrogen, through a silica tube containing iron filings heated to *ca.* 460°. A white solid (0.25 g) condensed in the cold trap and was identified, by comparison of the i.r. spectrum with that of an authentic sample,¹⁰ as perfluoro-4-phenylpyridine (70%).

Fluoride-ion Induced Reactions of Tetrafluoropyridazine.—(a) *With decafluorocyclohexene.* (i) At atmospheric pressure. A mixture of caesium fluoride (3.0 g, 19.7 mmol), tetrahydrothiophen dioxide (30 ml), tetrafluoropyridazine (3.8 g, 25.0 mmol), and perfluorocyclohexene (10.0 g, 38.2 mmol) was stirred vigorously under nitrogen at *ca.* 20° for 93 h.

The volatile material (8.3 g) was transferred, under high vacuum, to a cold trap and analytical scale g.l.c. (silicone elastomer on Celite; 150°) gave the yield of product (XII) (87% based on a 100% conversion of tetrafluoropyridazine). Samples were separated by preparative scale g.l.c.; perfluorocyclohexene was identified spectroscopically and *perfluoro-4-cyclohexylpyridazine* (XII) was obtained as a liquid, b.p. 200° at 760 mmHg (Found: C, 29.1; F, 64.7%; M^+ , 414. $C_{10}F_{14}N_2$ requires C, 29.0; F, 64.3%; M , 414); λ_{\max} (cyclohexane) 230 and 272 nm (ϵ 7403 and 6963); i.r. λ_{\max} 6.88, 7.12, 7.77, 7.91, 8.07, 8.20, 8.32, 8.45, 8.60, 9.80, 9.85, 10.40, and 12.51 μm ; δ_F 74.7 (3-F), 98.2 (6-F), and 182.3 ($-\text{CF}<$) and several complex signals at 115–144 p.p.m. (unassigned). The residual involatile material was worked up in the usual manner to give an oily residue (0.75 g). A solid (0.3 g) was sublimed (100° at 0.01 mmHg) from the residue and identified as a pyridazinone formed by hydrolysis of the product (XII), m.p. 251° (Found: C, 28.8; H, 0.34; F, 59.9%; M^+ , 412. $C_{10}HF_{13}N_2O$ requires C, 29.1; H, 0.24; F, 60.0%; M , 412); λ_{\max} (ethanol) 241 and 276 nm (ϵ 8900 and 5600); i.r. λ_{\max} 6.4, 7.36, 8.23, 8.40, 9.73, and 10.38 μm .

A similar reaction using caesium fluoride (3.0 g, 19.7 mmol), tetrahydrothiophen dioxide (30 ml), tetrafluoropyridazine (2.8 g, 18.6 mmol), and perfluorocyclohexene (11.4 g, 43.5 mmol) for 117 h at *ca.* 90° gave the monosubstituted derivative (XII) (4.5 g, 60%), identified by comparison of the i.r. spectrum with that of an authentic sample, as the major product. A small amount of solid (0.2 g) isolated from the involatile mixture was *perfluoro-3,5-dicyclohexylpyridazine* (XIII) (Found: C, 28.3; F, 67.0%; M^+ , 676. $C_{16}F_{24}N_2$ requires C, 28.40; F, 67.46%; M , 676); i.r. λ_{\max} 7.47, 7.52, 7.9, 8.01, 8.16, 8.31, and 10.28 μm ; δ_F 65.8 (6-F), 97.5 (4-F), and 182.2 and 186.3 ($-\text{CF}<$) and several signals at 110–149 p.p.m. (unassigned).

(b) *With octafluorocyclopentene.* Several reactions using caesium fluoride, tetrahydrothiophen dioxide, perfluorocyclopentene, and tetrafluoropyridazine at atmospheric pressure or in sealed tubes under a variety of conditions gave the dimer (XV) as the only significant product as well as reasonable recovery of the starting material.

(c) *With hexafluorocyclobutene.* Several reactions using caesium fluoride, tetrahydrothiophen dioxide, perfluorocyclobutene, and tetrafluoropyridazine at atmospheric pressure or in sealed tubes under a variety of conditions gave the trimer (XVIII) as the only significant product and reasonable recovery of the starting materials.

Dimerisation of Decafluorocyclohexene.—A mixture of caesium fluoride (3.0 g, 19.7 mmol), tetrahydrothiophen dioxide (40 ml), and perfluorocyclohexene (8.0 g, 30.5 mmol) was heated in a sealed tube for 65 h at *ca.* 170°. On cooling, the volatile material (6.5 g) was transferred, under vacuum, to a cold trap. Analytical scale g.l.c. (di-isodecyl phthalate on Celite; 50°) gave yields of products (XVIa) and (XVII) (19 and 57% respectively,

based on an 85% conversion of perfluorocyclohexene). Samples were separated by preparative scale g.l.c.; perfluorocyclohexene was identified spectroscopically and *perfluoro-(1-cyclohexylcyclohexene)* (XVIa) was obtained as a liquid, b.p. 161–162° at 760 mmHg (Found: C, 27.8; F, 72.9%; M^+ , 524. $C_{12}F_{20}$ requires C, 27.5; F, 72.5%; M , 524); i.r. λ_{\max} 7.59, 7.83, 7.98, 8.07, 8.22, 8.37, 8.56, 8.65, 8.72, 9.78, 10.19, and 10.34 μm ; δ_F 98.3 (1F, C=CF) and 181.9 (1F, $-\text{CF}<$) and numerous signals at 105–145 p.p.m. (unassigned). *Perfluorobicyclohex-1-enyl* (XVII) was also isolated as a liquid (Found: C, 29.3; F, 71.0%; M^+ , 486. $C_{12}F_{18}$ requires C, 29.6; F, 70.4%; M , 486); λ_{\max} (cyclohexane) 276 nm; i.r. λ_{\max} 7.47, 7.65, 7.73, 8.00, 8.22, 8.41, 8.49, 8.7, 9.73, and 19.85 μm ; δ_F 110.7 (4F), 113.2 (2F), 122.2 (4F), and 136.2 (8F) p.p.m.

A similar reaction for 70 h at *ca.* 150° gave dimer (XVIa) (78%) as the major product and only traces of dimer (XVII).

Dimerisation of Octafluorocyclopentene.—A mixture of caesium fluoride (3.0 g, 19.7 mmol), tetrahydrothiophen dioxide (20 ml), and perfluorocyclopentene (8.5 g, 40.0 mmol) was heated at *ca.* 125° for 20 h in a sealed tube. On cooling, the volatile products (7.3 g) were transferred, under high vacuum, to a cold trap; the products were distilled over the range 120–130°, and analysis of the distillate by g.l.c. (di-isodecyl phthalate on Celite; 100°) showed this to be a single compound identified as *perfluoro-bi(cyclopentylidene)* (XV) (86%), b.p. 127° at 760 mmHg (Found: C, 28.2; F, 72.1%; M^+ , 424. $C_{10}F_{16}$ requires C, 28.3; F, 71.7%; M , 424); i.r. λ_{\max} 7.59, 7.88, 8.32, 8.51, 9.23, 9.65, and 10.49 μm ; δ_F 110.1 and 136.1 p.p.m. (relative intensity 1 : 1).

Trimerisation of Hexafluorocyclobutene.—A mixture of caesium fluoride (5.0 g, 32.8 mmol), tetrahydrothiophen dioxide (20 ml), and perfluorocyclobutene (10.0 g, 61.7 mmol) was heated at *ca.* 125° for 24 h in a sealed tube. On cooling, the volatile material was transferred, under vacuum, to a cold trap and subsequently distilled over the range 140–150°. Analytical scale g.l.c. (di-isodecyl phthalate on Celite; 100°) showed the distillate to be a single compound identified as *perfluoro-1-[bi(cyclobutyl)-1-yl]cyclobutene* (XVIII) (6.7 g, 67%), b.p. 151° at 760 mmHg (Found: C, 29.6; F, 70.7%; M^+ , 486. $C_{12}F_{18}$ requires C, 29.6; F, 70.4%; M , 486); i.r. λ_{\max} 7.19, 7.56, 7.75, 8.08, 8.22, 8.42, 8.60, 9.86, and 10.04 μm ; δ_F 91.8 (1F, C=CF) and 173.0 (1F, $-\text{CF}<$), and several signals at 111–130 p.p.m. (unassigned).

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