

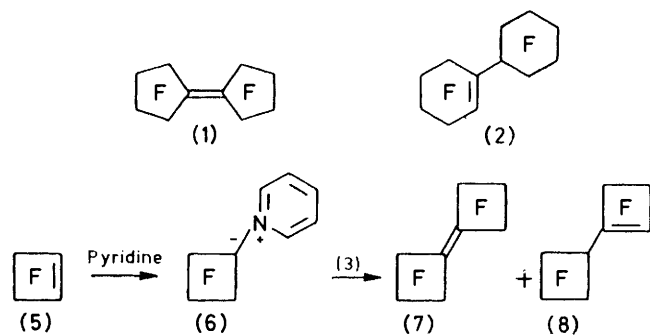
Reactions involving Fluoride Ion. Part 18.¹ Derivatives of Perfluorocycloalkenes

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Unlike perfluorocyclobutene, perfluorocyclo-pentene and -hexene do not form oligomers with pyridine. A range of oligomers is obtained from mixtures of perfluorocycloalkenes in reactions initiated by caesium fluoride. Products are also obtained from perfluorocycloalkenes with perfluoropropene and between perfluorocyclobutene and perfluorobut-2-ene. A variation is observed in the balance between *exo*- and *endo*-isomers of perfluorocycloalkene oligomers. It is concluded that conformational interactions dominate the position of equilibrium, except with four-membered rings, where angle strain is also important.

FLUORIDE-ION initiated reactions of cyclic fluoro-olefins provide a route to some fascinating oligomers of these systems.² We have previously³ obtained the dimers (1) and (2) of perfluorocyclo-pentene (3) and -hexene (4) respectively, using caesium fluoride in sulpholan, but the corresponding reaction with perfluorocyclobutene (5) gave mainly a trimer. Nevertheless, in the preceding paper, we have reported that the

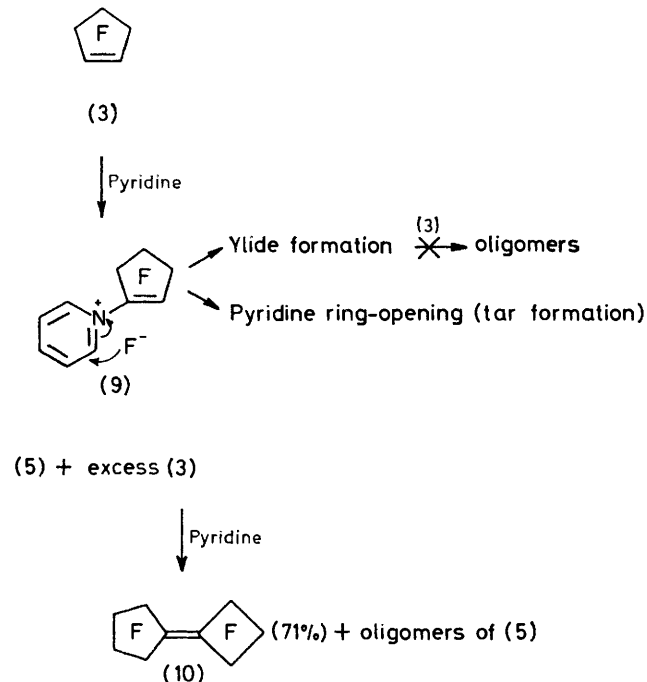


A fluorine symbol within a ring signifies that all unmarked positions in that ring are bonds to fluorine

dimers (7) and (8) may be obtained in reasonable yield in a process initiated by pyridine.^{1,4} Consequently, we have now investigated corresponding reactions of pyridine with perfluorocyclo-pentene (3) and -hexene (4), and perfluoro-but-2-ene, -propene, and -ethylene to determine whether pyridine provides advantages over fluoride ion as an initiator for oligomerisation of these systems. In all these cases, however, tar was produced, although with significant recovery of the fluoro-olefin, but no oligomers of the olefins could be detected. Therefore, perfluorocyclobutene (5) is unusual amongst fluoro-olefins in its reaction with pyridine but the reasons for this special behaviour are not clear. The dimers (7) and (8) are formed by reaction of the cycloalkene (5) with the derived ylide (6) and it is possible that with other fluoro-olefins, *e.g.* perfluorocyclopentene (3), the initial reaction product (9) undergoes pyridine ring-opening with fluoride ion, rather than further reaction through an ylide analogous to (6). Furthermore, only in one case have we been able to trap the ylide (6) with a fluoro-olefin other than (5). In the presence of excess of perfluorocyclopentene (3), perfluorocyclobutene (5)

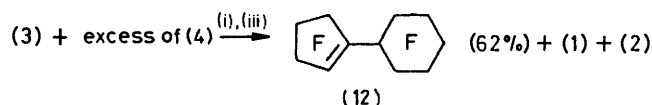
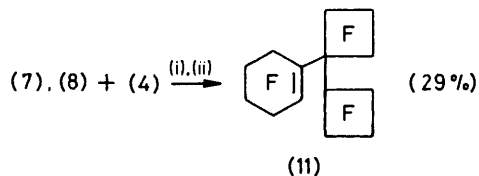
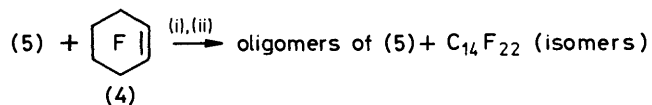
reacted with pyridine and gave a substantial amount of (10), in addition to oligomers of (5). A small amount of an isomer of (10) (*ca.* 5%) was detected but we have not isolated this compound. The structure of (10) follows very simply from the symmetry, as revealed by the ¹⁹F n.m.r. spectrum.

In contrast to the failure of pyridine to promote reactions between different perfluorocycloalkenes, or between these systems and other fluoro-olefins, a wide range of products may be obtained in corresponding reactions promoted by fluoride ion. All these reactions were carried out using dimethylformamide (DMF) as solvent and were initiated by anhydrous



caesium fluoride. Perfluorocyclo-butene (5) and -pentene (3) gave a complex mixture of products from which (10) could be isolated. In contrast, a corresponding reaction of (5) with perfluorocyclohexene (4) gave, largely, oligomers of (3), together with a small fraction containing isomers of C₁₄F₂₂. The major isomer (11) was prepared by an analogous reaction of the dimer

mixture (7),(8) with (4). Reaction of perfluorocyclopentene (3) with excess of perfluorocyclohexene (4) required a higher temperature but, in this case, the main product was (12), together with the dimers (1) and (2).

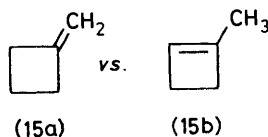
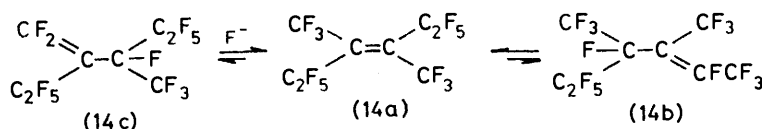
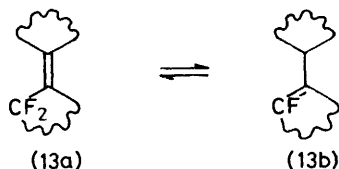


i, DMF, CsF; ii, room temperature; iii, 80 °C

We have now prepared a range of fluorinated cycloalkene derivatives containing two rings and these systems exhibit an interesting variation in the position of the double-bond between *exo*- and *endo*-positions, under

time of writing we are not aware of any report on equilibrium studies.

Factors which are most likely to affect the position of equilibrium in a fluorinated system corresponding to (13a and b) are (i) the presence, or otherwise, of a vinylic fluorine atom; (ii) the relative angle-strain energy for *exo*- (13a) versus *endo*- (13b) isomers; and (iii) the relative importance of conformational interactions of fluorine atoms in the two structures. Various observations indicate that vinylic fluorine atoms raise the energy of an olefinic system and this has been attributed to repulsive interaction of the non-bonding electrons of fluorine with those of the π -system.⁹ In accord with this is the fact that, in acyclic fluoro-olefins, the most stable isomer is invariably one which has the least number of fluorine atoms attached to the double bond. For example, olefin (14) exists almost exclusively in the form (14a) in the presence of fluoride ion.^{10,11} It is difficult to anticipate the relative importance of angle strain for (13a) and (13b), although Doering and his co-workers¹² have concluded that there is little difference in *total* strain energy between methylenecyclobutane (15a) and methylcyclobutene (15b), *i.e.* that the presence of two unsaturated sites is no more disadvantageous than one, in a four-membered ring. However, whether this is a balancing effect of lower angle strain in (15a) versus relief of conformational interactions in (15b) is not clear. The chemical effects of conformational interactions in five- and six-membered rings have been dis-



equilibrium control, *i.e.* in the presence of fluoride ion. Comparing the compounds (1), (2), (7), (8), (10), and (12), we see that compounds (2) and (12) are exclusively in the *endo*-form, whereas compound (1) is exclusively, and (10) at least 95%, in the corresponding *exo*-form. In contrast, the *exo*- and *endo*-isomers (7) and (8) occur in *ca.* equal amounts. A comparison with the position of equilibrium of the hydrocarbon systems analogous to (1), (2), (7), and (8) would be interesting but, although some of these systems have been synthesised,⁵⁻⁸ at the

cussed extensively^{13,14} and the following general points should be borne in mind. (i) Introduction of an unsaturated site into a five-membered ring will *decrease* eclipsing interactions while (ii) introduction of a single unsaturated carbon into a six-membered ring will move the interactions towards the eclipsing conformation. This being the case, then introduction of *two* unsaturated carbon atoms should be more favourable than introduction of one because the number of nearly-eclipsing interactions is diminished. On the basis of these effects

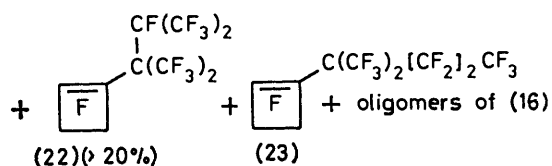
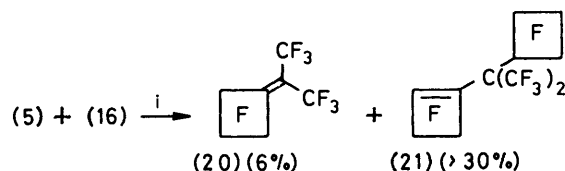
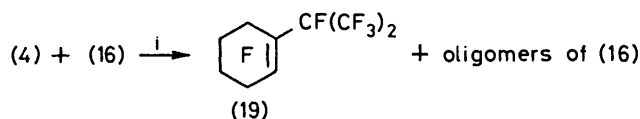
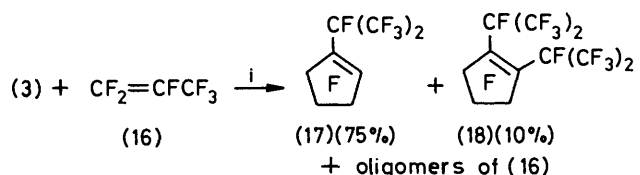
a rationale of the structures (1), (2), (7), (8), (10), and (12) may be advanced.

First, the structures (1) and (10), containing no vinylic fluorine atoms, may be seen as those which also minimise conformational interactions. The systems (2) or (12), containing a perfluorocyclohexyl group, clearly demonstrate that it is more favourable to *avoid* unsaturated sites in a six-membered ring [*i.e.* (12)] but that, where it is unavoidable, then it is better to have both sites in the

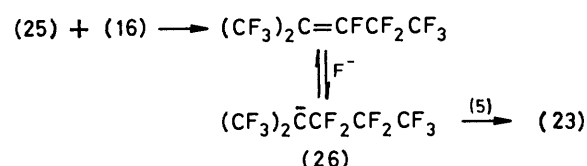
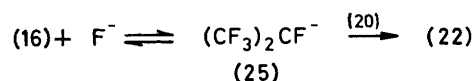
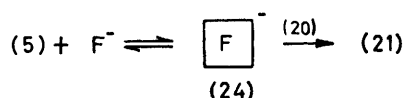
that having the carbon atoms of the double bond incorporated into *separate* four-membered rings [*i.e.* (7)] involves higher angle-strain than the alternate [*i.e.* (8)]. This is borne out by the much greater reactivity of (7) over analogous systems like (1) or (14a) and the novel chemistry of (7) will be described later.¹⁵

We have also investigated fluoride-ion induced reactions of perfluorocycloalkenes with perfluoropropene. Reactions with perfluorocyclopentene (3) and -hexene (4) are relatively straightforward and the products may be understood as involving attack by the perfluoroisopropyl anion on (3), giving both mono- (17) and di- (18) substitution (N.B. some perfluorodialkyl-cyclopentenes have also been made by other workers¹⁶), and on the less reactive perfluorocyclohexene (4), giving only mono-substitution (19). As explained earlier, the preferred *endo*-structures for (17)–(19) are consistent with minimising conformational interactions.

Perfluoro-propene and -cyclobutene are of comparable reactivity towards nucleophiles and, therefore, a more complicated reaction product is obtained than with (3) or (4);¹⁷ nevertheless, compounds (20)–(23) have been isolated and characterised (see Experimental section). These compounds, (20)–(23), arise from processes involving several intermediate anions, (24), (25), and (26), as indicated in the Scheme. Compounds (17), (18), and (19) have the *endo*-structure, which minimises conformational interactions in these systems, but compound (20) by contrast has the *exo*-structure. This difference is most likely due to the fact that isomer (20) is able to flex more freely (27),(28) to relieve eclipsing

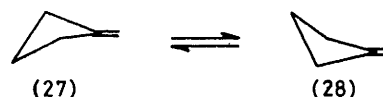


i, CsF, DMF, room temperature



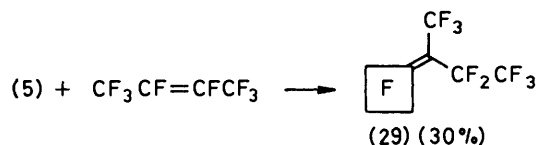
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same ring [*i.e.* (2)]. Formally, conformational effects should be very similar in (1) and (7) but the fact that (8) is of comparable energy to (7) can only be attributed to angle strain being a significant factor in raising the energy of (7) relative to (8). It seems clear, therefore,



interactions while the *endo*-isomer of (20) would, of course, be rigidly planar and eclipsing interactions would be at a maximum.

Reaction of perfluorocyclobutene (5) with the much less reactive perfluorobut-2-ene gave (29) as the main product and, here again, this exists exclusively as the *exo*-isomer.



On examination of the various structures described in this paper, where *exo*- and *endo*-isomers are possible it is clear that conformational aspects are the features dominating the position of equilibrium, rather than the presence, or otherwise, of a vinylic fluorine atom. This is wholly understandable because the importance of conformational interactions, even in hydrocarbon systems is well known,^{13,14} but, the larger size of fluorine,

together with the effects of considerable numbers of non-bonding electron-pairs, will make these effects even more dominant.

Structure Derivation.—Structures of the compounds described earlier generally follow simply from the ^{19}F n.m.r. spectra (see Experimental section). In all structures containing fluorine attached to unsaturated carbon, the $\text{F}-\text{C}=\text{C}$ resonance occurs to lower field than $-\text{CF}_2-$ signals in the spectrum. Furthermore, each of these structures contains a 'tertiary' fluorine atom >CF , which is associated with a signal at characteristically high field. Assignments are also supported by the infrared spectra where, in general, for a system $(\text{R}_\text{F})_2\text{C}=\text{C}(\text{R}_\text{F})_2$ (R_F = perfluoroalkyl), the intensity and frequency of $\nu(\text{C}=\text{C}$ str.) is lower than for $(\text{R}_\text{F})_2\text{C}=\text{CFR}_\text{F}$.¹⁸

EXPERIMENTAL

^{19}F N.m.r. spectra were recorded on a Varian A56/60D spectrometer with CFCl_3 as external standard; upfield shifts (p.p.m.) are quoted as positive. Molecular weights of pure compounds were determined using an AEI MS9 instrument. Laser-Raman spectra were recorded using a Carey 82 laser. G.l.c. was carried out using a Varian-aerograph 920 (gas density balance) and g.l.c.-m.s. using a Pye 104, linked to a V.G. micromass, mass spectrometer. Three columns were used: column A, 20% di-isodecylphthalate on Chromosorb P; Column O, 30% silicone SE30 on Chromosorb G60-80; and Column Z, 2-cyanoethylmethylsilicone on Chromosorb P. A Fischer-Spaltrohr HMS 500 column was used for distillation.

Reaction of Perfluorocyclobutene (5) and Perfluorocyclopentene (3) with Pyridine.—A mixture of pyridine (3.0 g, 38.0 mmol), perfluorocyclopentene (3) (33.3 g, 157.1 mmol), and perfluorocyclobutene (5) (25.2 g, 157.4 mmol) was stirred at room temperature for 30 h in a sealed tube which was then opened and the volatiles transferred, under high vacuum, to a cold-trap. Distillation using a small Vigreux column gave (3) (18.9 g) and the residue was washed with water, dried (P_2O_5), and transferred under vacuum to a cold-trap. The resultant liquid (27.9 g) was shown by g.l.c. (column O, 80 °C) to be a mixture of (3) (19%), perfluorobicyclobutylidene¹ (7) (15%), perfluorocyclobutylcyclobutene¹ (8) (13%), and perfluoro-1,2-dicyclobutylcyclobutene¹ (12%); one additional peak was subsequently shown to be a mixture of C_9F_{14} isomers (41%).

The liquid was distilled and the fraction boiling at 103–104 °C shown to be a mixture of two isomers (ca. 20 : 1 ratio) [g.l.c.-m.s. (column Z)]. A sample of the major isomer was separated by preparative g.l.c. and identified as *perfluorocyclobutylidenecyclopentene* (10) [71% yield based on (3) consumed]. Compound (10) (Found: C, 28.7; F, 70.6%; M^+ , 374 (very weak). C_9F_{14} requires C, 28.88; F, 71.12%; M , 374) showed i.r. (gas) λ_{max} 7.77, 8.19, 8.48, 9.49, and 10.57 μm ; Raman, $\text{C}=\text{C}$ at 5.72 μm ; δ_F 136.9 (4 F, cyclopentyl ring), 132.1 (2 F, cyclobutyl ring), 117.1 (4 F, cyclobutyl ring), and 114.2 (4 F, cyclopentyl ring).

It was concluded from the results of several reactions that the yield of compound (10) increased with an increasing initial concentration of (3).

Reactions of Perfluorocyclobutene (5) and Other Perfluoroalkenes with Pyridine.—Reactions were carried out with mixtures containing pyridine, perfluorocyclobutene (5),

and the following olefins: perfluoro-propene, -but-2-ene and -cyclohexene. In no case could co-oligomers be detected and in each case the expected oligomer mixture from reaction of (5) with pyridine was obtained, together with a good recovery of the other perfluoroalkene.

Reactions of Other Perfluoroalkenes with Pyridine.—Reactions were carried out between pyridine and the following perfluoroalkenes under the conditions stated: perfluoroethylene (100 °C, 2 h), -propene (room temperature, 48 h), -but-2-ene (room temperature, 48 h), -cyclopentene (80 °C, 24 h), and -cyclohexene (95 °C, 24 h). No oligomers were detected and, in each case, there was a good recovery of the perfluoroalkene, although accompanied by some formation of tar.

Fluoride-ion Induced Co-oligomerisations.—*Perfluorocyclobutene (5) with perfluorocyclopentene (3).* A mixture of compounds (5) (8.4 g, 51.9 mmol) and (3) (10.5 g, 49.5 mmol), caesium fluoride (4.5 g, 29.6 mmol), and DMF (20 ml) was stirred at atmospheric pressure and room temperature for 150 h. Volatile material was transferred, under high vacuum, to a cold-trap, and the lower fluorocarbon layer was removed, washed with water, dried (P_2O_5), and transferred under vacuum to a cold-trap. The resultant liquid (15.8 g) was shown [analytical g.l.c. (column O)] to be a highly complex mixture: a C_9F_{14} fraction was separated by a combination of fractional distillation and preparative g.l.c. (column O) and shown [^{19}F n.m.r. and g.l.c. (column Z)] to be almost identical with the C_9F_{14} fraction [95% compound (10)] from the corresponding co-oligomerisation with pyridine. G.l.c.-m.s. indicated the major product of the reaction mixture to be a mixture of $\text{C}_{13}\text{F}_{20}$ isomers.

Perfluorocyclobutene (5) with perfluorocyclohexene (4). A mixture of compounds (5) (19.4 g, 119.8 mmol) and (4) (25.8 g, 98.5 mmol), caesium fluoride (6.3 g, 41.5 mmol), and DMF (20 ml) was stirred at room temperature and atmospheric pressure for 48 h. Volatile material was transferred, under vacuum, to a cold-trap; the lower fluorocarbon layer was removed, washed with water, dried (P_2O_5), and transferred under vacuum to a cold-trap. The resultant liquid (40.2 g) was shown [g.l.c. (column O, 90 °C)] to be a mixture containing compound (4) and oligomers from compound (5); one other major peak was subsequently identified (g.l.c.-m.s.) as a $\text{C}_{14}\text{F}_{22}$ fraction. This fraction was purified by a combination of fractional distillation and preparative g.l.c. and the resultant liquid (1.1 g) was shown to be a mixture of isomers (Found: C, 28.9; F, 71.8%; $\text{C}_{14}\text{F}_{22}$ requires C, 28.67; F, 71.33%).

Perfluorocyclobutylcyclobutene (7),(8) with perfluorocyclohexene (4). A mixture of compounds (7),(8) (1.41 g, 4.35 mmol) and (4) (3.68 g, 14.04 mmol), caesium fluoride (2.72 g, 17.9 mmol), and DMF (10 ml) was stirred for 120 h at room temperature. Volatile material was transferred, under vacuum, to a cold-trap; the lower fluorocarbon layer was removed, washed with water, dried (P_2O_5), and transferred under vacuum to a cold-trap. The resultant liquid (4.17 g) was shown [g.l.c. (column O)] to be a mixture of compounds (7), (8), and (4) together with one other major component and several trace components, which were unidentified. The major new component was separated by preparative g.l.c. and the resultant low-melting solid (0.74 g) shown to be a single $\text{C}_{14}\text{F}_{22}$ isomer, *perfluoro-1-cyclobutyl-1-cyclohex-1-en-1-ylcyclobutane* (11) (29% yield). Compound (11) (Found: F, 70.9%; M^+ 586. $\text{C}_{14}\text{F}_{22}$ requires F, 71.33%; M 586) showed i.r. λ_{max} 5.87, 7.04, 7.18, 7.58, 7.63, 7.78,

7.91, 8.03, 8.14, 8.40, 8.55, 8.87, 9.78, 10.00, 12.67, and 13.04 μm ; δ_{F} 181.0 (1 F, >CF), 86.8 (1 F, =C-F), and signals between 110 and 142 (20 F, unassigned).

Compound (11) was identified as the major isomer present in the $\text{C}_{11}\text{F}_{22}$ fraction from the reaction of (4) and (5) with caesium fluoride, by comparison of n.m.r. spectra.

Perfluorocyclopentene (3) with perfluorocyclohexene (4). A mixture containing compounds (3) (8.1 g, 38.2 mmol) and (4) (13.6 g, 51.9 mmol), caesium fluoride (5.8 g, 38.2 mmol), and DMF (20 ml) was stirred in a sealed tube at ca. 80 °C for 120 h. The tube was opened and the volatile material transferred, under vacuum, to a cold-trap. The lower fluorocarbon layer was removed, washed with water, dried (P_2O_5), and transferred under vacuum to a cold-trap. The resultant liquid (19.2 g) was shown [g.l.c. (column Z)] to be a mixture of compounds (3) (36%), (1) (17%), (2) (8%), and one other component (39%) subsequently identified as *perfluorocyclohexylcyclopentene* (12).

Compounds (1) and (3) were removed from the mixture by fractional distillation and the residue separated by preparative g.l.c. to give compound (12) (Found: C, 27.6; F, 72.6%; M^+ , 474. $\text{C}_{11}\text{F}_{18}$ requires C, 27.85; F, 72.15%; M , 474); i.r. λ_{max} 5.85, 7.15, 7.49, 7.57, 7.62, 7.71, 7.87, 8.00, 8.19, 8.47, 9.35, 9.71, 10.10, 10.31, and 13.51 μm ; δ_{F} 187.4 (1 F, >CF), 108.3 (1 F, very broad, =C-F), 107.3 (2 F, cyclopentenyl ring), and signals between 115 and 148 (14 F, unassigned).

Perfluorocyclopentene (3) with perfluoropropene. A mixture of compounds (3) (9.6 g, 45.3 mmol) and (16) (9.4 g, 62.7 mmol), caesium fluoride (5.6 g, 36.9 mmol), and DMF (30 ml) was stirred for 3 h at atmospheric pressure and room temperature. Volatile material was transferred under vacuum to a cold-trap. The lower fluorocarbon layer was removed, washed with water, dried (P_2O_5), and transferred under vacuum to a cold-trap. The resultant liquid (17.9 g) was shown [g.l.c. (column O)] to be a mixture of several components. Fractional distillation gave compound (3) (2.1 g) containing traces of compound (16) and its dimer; a fraction (9.8 g, b.p. 83–84 °C, identified as *perfluoroisopropylcyclopentene* (17); and a residue (4.3 g) shown (g.l.c.) to be a mixture of compound (17), trimers of compound (16), and one other compound subsequently identified as *perfluoro-1,2-di-isopropylcyclopentene* (18); this was separated by preparative g.l.c. to give the pure compound (1.9 g). Yields of compounds (17) and (18) were ca. 74 and ca. 10% respectively, based on compound (3) consumed. Compound (17) (Found: F, 73.8%; M^+ , 372. C_9F_{14} requires F, 73.48%; M , 372) showed i.r. (gas) λ_{max} 7.12, 7.63, 7.69, 7.88, 7.96, 8.17, 8.35, 8.42, 8.54, and 10.15 μm ; δ_{F} 77.1 (6 F, two overlapping d of q), 107.5 (2 F, br m, C-5-F), 111.4 (1 F, br, =CF-), 122.1 (2 F, d, J 15 Hz, C-3-F), 132.4 (2 F, C-4-F), and 189.2 (1 F, septet, J 9 Hz >CF). Compound (18) (Found: C, 25.9; F, 74.7%; M^+ , 512. $\text{C}_{11}\text{F}_{20}$ requires C, 25.78; F, 74.22%; M , 512); i.r. (gas) λ_{max} 7.69, 7.87, 7.97, and 8.47 μm ; the ^{19}F n.m.r. spectrum showed this compound to be a mixture of rotamers at room temperature, δ_{F} (rotamer A) 169.0 (2 F, s, >CF), 137.2 (2 F, C-4-F), and 110.6 (4 F, C-3- and C-5-F), the CF_3 resonance(s) overlapping with those from rotamer B; δ_{F} (rotamer B) 175.8 (1 F, s, J 47 Hz, >CF), 170.5 (1 F, t, J 47 Hz, >CF), 136.7 (2 F, C-4-F), 111.4 (2 F, br s, C-5-F), 109.6 (2 F, d, J 47 Hz, C-3-F), 72.7 (6 F, d, J 47 Hz, CF_3 groups on isopropyl C-2), and ca. 73.7 (signal contains CF_3 groups for rotamer

A). Integration indicates that the rotamer ratio A : B is ca. 2 : 5.

Perfluorocyclohexene (4) with Perfluoropropene. A mixture of compounds (4) (12.7 g, 48.5 mmol) and (16) (12.3 g, 82.0 mmol), caesium fluoride (7.1 g, 46.7 mmol), and DMF (30 ml) was stirred at room temperature for 6 h at atmospheric pressure. Volatile material was transferred to a cold-trap under vacuum. The lower fluorocarbon layer was removed, washed with water, dried (P_2O_5), and transferred under vacuum to a cold-trap. The resultant liquid (23.7 g) was shown [g.l.c. (columns A and O)] to be a mixture of compound (4), oligomers of compound (16), and one other component, subsequently identified as *perfluoroisopropylcyclohexene* (19). ^{19}F N.m.r. of the mixture indicated that compound (19) was the major component. Compound (19), purified by a combination of fractional distillation and preparative g.l.c. (column A) (Found: F, 74.0%; M^+ , 412. C_9F_{16} requires F, 73.79%; M , 412) had b.p. 108–109 °C; i.r. (gas) λ_{max} 7.63, 7.89, 8.00, 8.33, 8.69, 9.26, 9.71, 10.12, and 10.29 μm ; δ_{F} 186.4 (1 F, J 37 Hz, >CF), 138.6 and 137.1 (each 2 F, C-4 and C-5-H), 123.5 (2 F, C-3-F), 110.3 (2 F, d, J 37 Hz, C-6-F), 107.2 (1 F, br, =CF-), and 78.3 p.p.m. (6 F, d of q, J_{D} 25, J_{Q} 4 Hz, CF_3).

Perfluorocyclobutene (5) with perfluoropropene. A mixture of compounds (5) (18.3 g, 113.0 mmol) and (16) (17.2 g, 114.7 mmol), caesium fluoride (8.7 g, 57 mmol), and DMF (20 ml) was stirred for 3 h at room temperature and atmospheric pressure. Volatile material was transferred out, under vacuum, to a cold-trap. The lower fluorocarbon layer was removed, washed with water, dried (P_2O_5), and transferred under vacuum to a cold-trap. The resultant liquid (33.2 g) was shown by g.l.c.–m.s. (column O) to be a highly complex mixture containing compound (21), $\text{C}_{11}\text{F}_{18}$ (>30%), compound (22), $\text{C}_{10}\text{F}_{18}$ (>20%), compound (23), $\text{C}_{10}\text{F}_{18}$, compound (20), C_7F_{12} , oligomers of compound (16), and trace amounts of material with mol. wt. > 500, which were not identified.

Fractional distillation gave compound (20) (2.1 g), b.p. 68–69 °C; a small intermediate fraction, b.p. 69–113 °C; and various intermediate fractions, b.p. 113–141 °C, shown (g.l.c.) to be mixtures of compounds (21), (22), and (23), and trimers of compound (16) in varying proportions. Samples of compounds (21), (22), and (23) were obtained by preparative g.l.c. from enriched distillation fractions.

Compound (20), *perfluoroisopropylidenecyclobutane* (Found: F, 72.5%; M^+ , 312. C_7F_{12} requires F, 73.08%; M , 312), showed i.r. (gas) λ_{max} 7.79, 7.89, 8.20, and 9.48 μm ; δ_{F} 65.3 (6 F, two overlapping q, J 7 Hz), 116.9 (4 F, m), and 132.4 (2 F). Compound (23), *perfluoro-2-cyclobut-1-en-1-yl-2-methylpentane*, b.p. 112 °C (Found: F, 73.4%; M^+ , 462. $\text{C}_{10}\text{F}_{18}$ requires F, 74.03%; M , 462), showed i.r. λ_{max} 7.04, 7.81, 8.00, 8.16, 8.26, 8.36, 8.62, and 10.40 μm ; Raman spectrum, C=C absorption at 5.84 μm ; δ_{F} 64.8 [6 F, $2 \times \text{>C}(\text{CF}_3)$], 83.0 (3 F, CF_3 of C_3F_7), 95.7 (1 F, =CF-), and 109.2, 115.3, 123.9, and 125.4 (each 2 F, unassigned). Compound (22), *perfluoro-2-cyclobut-1-en-1-yl-2,3-dimethylbutane*, b.p. 120 °C (Found: F, 74.4%; M^+ , 462. $\text{C}_{10}\text{F}_{18}$ requires F, 74.03%; M , 462), showed i.r. λ_{max} 7.01, 7.63, 7.75, 7.91, 8.08, 8.23, and 8.56 μm ; Raman spectrum, C=C absorption at 5.84 μm ; δ_{F} 63.4 [6 F, $2 \times \text{>C}(\text{CF}_3)$], 72.0 [6 F, $2 \times (\text{CF}_3)\text{CF}$], 95.5 (1 F, =CF-), 171.2 (1 F, >CF), and 115.1 and 124.5 (each 2 F, unassigned). Com-

pound (21), *perfluoro-2-cyclobut-1-en-1-yl-2-cyclobutylpropane*, b.p. 140 °C (Found: F, 71.9%; M^+ , 474. $C_{11}F_{18}$ requires F, 72.15%; M , 474), showed i.r. λ_{\max} 7.00, 7.55, 7.63, 7.69, 7.75, 8.00, 8.08, 8.12, 8.24, and 8.57 μm ; Raman spectrum, C-C absorption at 5.84 μm ; δ_F 65.4 (6 F, 2 overlapping q of d, J_D 5 Hz, J_Q 13 Hz), 91.2 (1 F, =CF-), 179.9 (1 F, >CF), 114.1 and 124.0 (each 2 F in cyclobutenyl ring), 130.3 and 134.2 (4 F, AB, J 223 Hz), and 130.5 (2 F in cyclobutyl ring).

A similar reaction using acetonitrile as solvent gave a mixture of compounds (22) (>50%) and (21) (>40%) with minor amounts of other co-oligomers.

Perfluorocyclobutene (5) and *perfluorobut-2-ene*. A mixture containing compounds (5) (18.9 g, 116.7 mmol) and (27) (21.0 g, 105 mmol), caesium fluoride (6.0 g, 39.5 mmol), and DMF (30 ml) was stirred at room temperature and atmospheric pressure for 10 days. Gaseous material (8.1 g) was removed and shown (i.r.) to be a mixture of compounds (5) and (27). Volatile material was then transferred, under vacuum, to a cold-trap. The lower fluorocarbon layer was removed, washed with water, dried (P_2O_5), and transferred under vacuum to a cold-trap. Distillation gave a fraction (12.1 g), b.p. 75–85 °C, shown by ^{19}F n.m.r. to be mainly (ca. 80%) *perfluoro-(1-methylpropylidene)-cyclobutane* (29), containing small amounts of compounds (7), (8), and traces of the dimer of compound (27). The residue (3.7 g) was shown by g.l.c.-m.s. to consist mainly of two $C_{12}F_{20}$ isomers. A pure sample of compound (29) was obtained by a combination of repeated fractional distillation and preparative g.l.c. (columns O and Z) (Found: C, 26.3; F, 73.2%; M^+ , 362. C_8F_{14} requires C, 26.52; F, 73.48%; M , 362), b.p. 85–86 °C, i.r. (gas) λ_{\max} 7.81, 7.93, 8.06, 8.19, and 9.18 μm , Raman spectrum, C=C absorption at 5.87 μm ; δ_F 63.0 (3 F, =C-CF₃), 84.7 (3 F, CF₂CF₃), 116.8 (2 F, q of m, J_Q 13 Hz, CF₂CF₃), 114.8 (4 F, cyclobutyl ring), and 132.6 (2 F, cyclobutyl ring).

A similar reaction at ca. 70 °C gave a much greater

proportion of higher molecular-weight material and little of (28).

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