

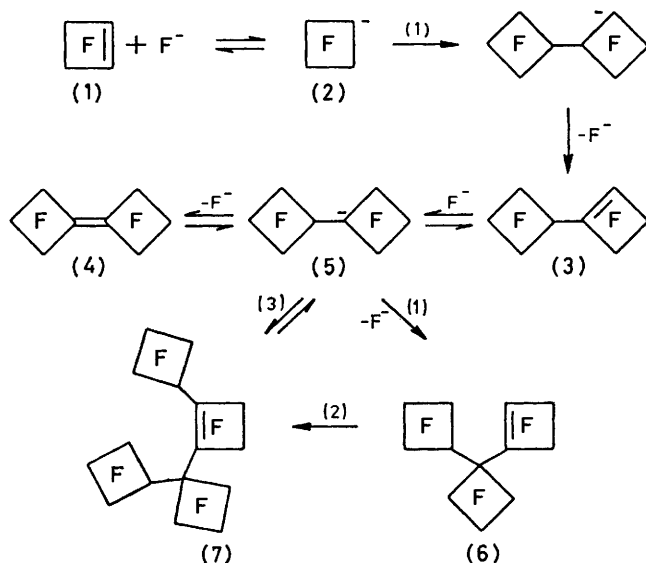
Reactions involving Fluoride Ion. Part 17.¹ Oligomers of Perfluorocyclobutene

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Reaction of perfluorocyclobutene (1) with fluoride ion gives mainly a trimer (6) together with dimers (3) and (4) and a tetramer (7). The tetramer (7) is also obtained directly from the dimers (3) and (4). Reaction of (1) with pyridine provides a useful route to dimers (3) and (4) and a different trimer (10). The structures of these oligomers have been established and mechanisms for their formation are presented.

IN this series of papers we are describing various fluoride-ion induced processes that build up synthetically useful molecules from relatively accessible unsaturated fluorocarbons. We have previously described oligomerisation reactions of cyclic perfluoroalkenes² but, with perfluorocyclobutene, we obtained predominantly a trimer (6). We now describe the development of a useful synthesis of the very interesting dimers (3) and (4). These target compounds are especially interesting in view of their strain and susceptibility to nucleophilic attack.

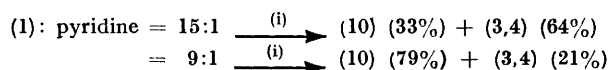
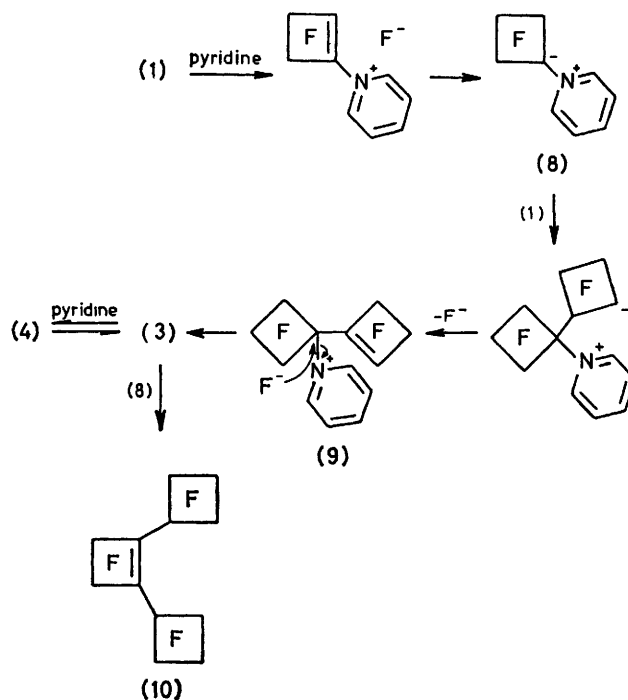


SCHEME 1 A fluorine symbol within a ring signifies that all unmarked positions in that ring are bonds to fluorine

Oligomerisation of perfluorocyclobutene with pyridine has also been studied by Pruett and his co-workers³ and reactions with fluoride ion have also been investigated by Fraticelli⁴ but the dimers (3) and (4) are not characterised in the literature. Following our earlier work on the reaction of (1) with fluoride ion,² we have attempted to modify the reaction conditions in order to obtain predominantly the dimers (3) and (4). However, over a very wide range of reaction conditions (see Experimental section) in all the reactions initiated by fluoride ion, we have always observed the trimer (6) as the main product.

The structure of the trimer (6) has been established previously² and the structures of the dimers (3) and (4)

follow very simply from their ¹⁹F n.m.r. spectra. The symmetrical dimer (4) shows only two fluorine resonances, while the unsymmetrical isomer (3) is characterised by the presence of resonances attributable to a single vinylic fluorine and a single 'tertiary' fluorine atom.



(i) Room temperature.

SCHEME 2

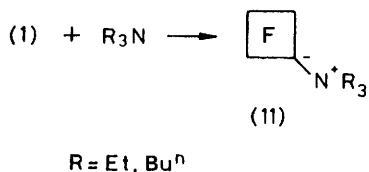
The structure of the tetramer (7) follows from the fact that it may also be obtained by dimerisation of (3) and (4), in the presence of a deficiency of fluoride ion, and the ¹⁹F n.m.r. spectrum of (7) is consistent with this structure.

We have re-investigated the reaction of (1) with pyridine,³ hoping to obtain a higher yield of the dimers (3) and (4) in this process and this has, in fact, provided a very useful route to these dimers. The composition of the reaction product depends critically on the proportion of pyridine to (1) used and on the reaction conditions. In fact the reactions are very difficult to reproduce

exactly but two typical results are shown in Scheme 2. We were completely surprised, however, to discover that the trimer (10) obtained in this reaction has a completely different structure from the trimer (6) described earlier. The symmetry, and hence the structure of (10), follows simply from the ^{19}F n.m.r. spectrum.

Products from the fluoride-ion induced reaction may be rationalised according to the mechanism outlined in Scheme 1. The dimers (3) and (4) are now known to react with fluoride ion to produce a relatively stable anion (5)⁵ and, consequently, further oligomerisation involving (3) and (4) occurs *via* this anion (5). The production of only small amounts of the tetramer (7), in the oligomerisation, occurs because displacement of the anion (5) from (7) occurs readily, although (7) may be obtained in good yield from (3) and (4) as described earlier.

Burton and his co-workers⁶ have, recently, shown that stable ylides (11) may be obtained from (1) with tertiary amines and it seems clear, therefore, that an analogous ylide (8) is formed as a reactive intermediate, with pyridine. The formation of the trimer (10) is then understandable by a mechanism outlined in Scheme 2. Fur-



ther evidence was obtained by a reaction of (1) with pyridine in the presence of (3) and (4). An amount of the trimer (10) was obtained that is in excess of the amount that could have been produced solely from (1). This demonstrates, therefore, that an ylide (8) did indeed react with (3) to produce (10). It is difficult to understand, however, why the trimer (10) is formed exclusively in the reaction involving pyridine while none of the isomer (6) could be detected. The mechanism outlined in Scheme 2 involves fluoride salts as intermediates; nevertheless, the fluoride ion cannot be available to (3) and (4), otherwise the ion (5) and, consequently, (6) would result. It follows, therefore, that the processes in Scheme 2 which involve loss of fluoride ion and subsequent reactions, *e.g.* to give (8) or the displacement of pyridine from (9), must be essentially concerted.

Work is progressing on the highly novel chemistry of these oligomers.

EXPERIMENTAL

^{19}F N.m.r. spectra were recorded on a Varian A56/60B spectrometer with CFCl_3 as external standard; upfield shifts (p.p.m.) are quoted as positive. Molecular weights of pure compounds were determined by mass spectrometry using an AEI MS9 instrument. Laser-Raman spectra were recorded using a Carey 82 laser. Analytical g.l.c. was carried out using a Varian-aerograph 920 (gas density balance detector). The approximate composition of mixtures was calculated assuming linear response of the

detector. Two columns (6 ft) were used: column O 30% silicone SE30 on Chromosorb G 60—80; and column Z, 2-cyanoethylmethylsilicone on Chromosorb P. A Fischer-Spaltrohr HMS 500 column was used for distillation.

Reaction of Perfluorocyclobutene (1) with Pyridine.—A mixture of pyridine (1.2 g, 15.2 mmol) and perfluorocyclobutene (38.0 g, 234.6 mmol) was stirred at room temperature in a sealed tube for 130 h. The volatile products were transferred under high vacuum to a cold-trap, washed with water (20 ml), dried (P_2O_5), and then transferred, under high vacuum, to a cold-trap. The resultant liquid (30.8 g, 81% recovery) was shown by analytical g.l.c. (column O 80 °C and column Z 60 °C) to be a four-component mixture, subsequently identified as consisting of perfluorocyclobutene (1) (3%), *perfluorobicyclobutylidene* (4) (35%), *perfluoro-1-cyclobutylcyclobutene* (3) (29%), and *perfluoro-1,2-dicyclobutylcyclobutene* (10) (33%). Distillation gave fractions boiling at 79—80 °C, pure compound (4); 80—84 °C, a mixture of compounds (3) and (4); 84—85 °C, pure compound (3); 85—146 °C (small), a mixture of compounds (3) and (10); and 147—148 °C, pure compound (10). Compound (4) (Found: F, 70.6%; M^+ , 324. C_8F_{12} requires F, 70.37%; M , 324) showed i.r. (gas) λ_{max} 7.28, 7.75, 8.16, 8.76, and 10.66 μm ; a Raman spectrum indicated C=C str. at 5.68 μm ; δ_{F} 117.8 (8F) and 132.0 (4F). Compound (3) (Found: F, 70.8%; M^+ , 324. C_8F_{12} requires F, 70.37%; M , 324) showed i.r. (gas) λ_{max} 7.45, 7.69, 7.76, 7.78, 8.09, 8.18, 8.31, 8.53, 10.67, and 5.78 (C=C str.) μm ; δ_{F} 98.5 (1F, C=CF), 189.6 (1F, >CF), 116.5 (2F), 121.7 (2F), 128.3 and 134.3 (4F, AB, J 232 Hz), and 131.1 and 134.7 (2F, AB, J 232 Hz). Compound (10) (Found: F, 70.0%; M^+ , 486. $\text{C}_{12}\text{F}_{18}$ requires F, 70.37%; M , 486) showed i.r. λ_{max} 7.10, 7.40, 7.66, 7.89, 8.08, 8.54, 10.50, 10.83, and 5.99 (weak C=C str.) μm ; a Raman spectrum indicated C=C str. at 6.01 μm ; δ_{F} 112.6 (4F), 127.0 and 133.0 (8F, AB, J 232 Hz), 130.3 and 134.0 (4F, AB J 230 Hz), and 180.0 (2F, >CF).

A similar reaction for 15 h between pyridine (2.1 g, 26.6 mmol) and (1) (38.0 g, 234.6 mmol) gave a mixture containing (4) (11%), (3) (10%), and (10) (79%), with a 67% recovery of fluorocarbon.

Reaction of Pyridine with a Mixture containing Perfluorocyclobutene (1) and the Dimers (3) and (4).—A mixture of perfluorocyclobutene (3.41 g, 21.0 mmol), compounds (3) and (4) (3.35 g, 10.3 mmol), and pyridine (0.6 g, 7.6 mmol) was stirred at room temperature for 6 h. The volatile products were transferred, under high vacuum, to a cold-trap and the upper pyridine layer removed. The residue (5.94 g) was shown by analytical g.l.c. (column O) to be a mixture of compounds (3) and (4) (32%) and compound (10) (68%).

Reactions of Dimers (3) or (4) with Pyridine.—A mixture of pyridine (2 drops) and compound (4) (0.41 g, 1.27 mmol) was stirred for 10 min at room temperature. Analytical g.l.c. (col. O) showed the resultant fluorocarbon layer to be an equilibrium mixture of compounds (3) and (4) (*ca.* 9 : 11). A similar reaction with compound (3) gave an identical ratio of compounds (3) and (4).

Reactions of Perfluorocyclobutene (1) with Caesium and Potassium Fluorides.—A nickel tube containing a mixture of perfluorocyclobutene (38.9 g, 240.1 mmol), caesium fluoride (6.2 g, 4.1 mmol), and dimethylformamide (DMF) (30 ml) was rotated at room temperature for 72 h. The volatile products were removed to a cold-trap, under high

vacuum, and the lower fluorocarbon layer was removed, washed with water, dried (P_2O_5), and then transferred under vacuum to a cold-trap. The resultant liquid (36.7 g) was shown by analytical g.l.c. (columns O and Z) to be a mixture of compounds (3) and (4) (21%), compound (6) (67%), compound (7), subsequently identified as *perfluoro-1-(1-cyclobutylcyclobutyl)-2-cyclobutylcyclobutene* (8%), and a compound (4%) identified (g.l.c.-m.s.) as a $C_{12}F_{18}$ isomer but, as yet, uncharacterised. Compounds (3), (4), and most of (6) were removed by fractional distillation and identified by comparison (n.m.r. and i.r. spectra) with authentic samples. The pot residue consisted of compounds (6) and (7) and these were separated by preparative g.l.c. (column O). Analytical g.l.c. showed that compound (7) contained a minor impurity identified by g.l.c.-m.s. (column Z) as $C_{16}F_{22}$ (defluorinated material) (<5%). This was removed by preparative g.l.c. to give pure compound (7) (Found: C, 29.7; F, 69.9%; M^+ 648. $C_{16}F_{24}$ requires C, 29.63; F, 70.37%; M , 648), i.r. λ_{max} 7.18, 7.20, 7.41, 7.82, 8.13, 8.26, 8.61, 9.03, 9.92, 10.09, 10.74, 10.96, and 12.59 μm ; δ_F 183.1 (1 F, d, J 62 Hz, >C-F), 175.3 (1 F, d, J 62 Hz >C-F), and signals between 110 and 138.0 (22 F, unassigned).

Fluoride-ion induced reactions of perfluorocyclobutene (1) were carried out under a variety of conditions. 2,5,8,11,14-Pentaoxapentadecane (tetraglyme) as solvent produced similar results as those obtained using DMF; using tetrahydrothiophen dioxide, the reaction proceeded slowly at 50 °C to give mainly (>95%) compound (6); whilst, using acetonitrile as solvent, oligomerisation was either very slow or did not occur at room temperature. The reaction was slow at room temperature when potassium fluoride was used instead of caesium fluoride as initiator.

Dimerisation of Compounds (3) and (4).—A mixture of caesium fluoride (0.31 g, 2.04 mmol) and compounds (3) and (4) (3.11 g, 9.60 mmol) was stirred for 100 h in DMF (10 ml) at room temperature. The volatile products were trans-

ferred, under high vacuum, to a cold-trap and the lower fluorocarbon layer was removed, washed with water, dried (P_2O_5), and transferred to a cold-trap under vacuum. The resultant liquid (2.43 g) was shown by analytical g.l.c. (column O) to be essentially a mixture of compounds (3) and (4) and two other compounds. These were identified by g.l.c.-m.s. as a tetramer, $C_{16}F_{24}$ (ca. 80%), and another compound, $C_{16}F_{22}$ (ca. 5%). A sample of the tetramer was isolated by preparative g.l.c. and identified as compound (7) by comparison of spectra.

Reaction of Compound (7) with Caesium Fluoride.—A mixture of compound (7) (0.72 g, 1.11 mmol) and excess of caesium fluoride in DMF (5 ml) was stirred during 24 h at room temperature. The volatile products were transferred under vacuum to a cold-trap and the lower fluorocarbon layer (0.47 g) was removed. This was shown by analytical g.l.c. and i.r. spectroscopy to be a mixture containing mainly compounds (3) and (4).

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