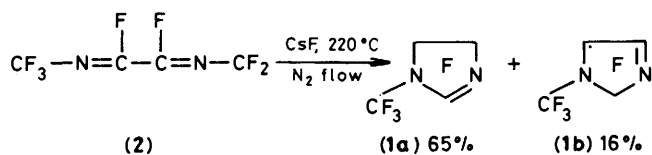# Reactions Involving Fluoride Ion. Part 31.[1] Co-oligomers of Perfluoro-1-methyl-1,3-diazacyclopent-2- and -3-ene

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The fluoride ion-induced co-oligomerisations of perfluoro-1-methyl-1,3-diazacyclopent-2- and -3-ene (1) with hexafluoropropene and perfluoro-cyclobutene, -cyclopentene, and -cyclohexene are reported. Comparisons are made between these reactions of nitrogen anions and the corresponding chemistry of fluorinated carbanions.

In this series of papers, we are developing an analogy between the role of fluoride ion, in reactions with unsaturated fluorocarbons, and the proton, in its reactions with unsaturated hydrocarbons, Indeed, there is now an extensive chemistry of polyfluorocarbanions generated in this way, including oligomerisation of perfluoro-alkenes and -cycloalkenes, and polyfluoroalkylation reactions.[2] Recently, we have extended our investigations to nitrogen anion chemistry, derived from fluorinated azacyclohexane derivatives[3] and from perfluoro-2,5-diazahexa-2,4-diene (2).[4] The development of a high-yield synthesis of perfluoro-1-methyl-1,3-diaza-cyclopent-2- and -3-ene (1) from (2)[4] now allows us to extend the chemistry of derived nitrogen anions to include co-oligomerisation reactions and to make some comparisons of the chemistry of fluorinated nitrogen anions and carbanions.
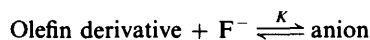
of perfluoro-2-azapropene with perfluoro-isobutene and -cyclobutene.[6]

We need to remember that, in these reactions, the overall rate constant for the reaction of an anion, generated by fluoride, with an olefin derivative, will be the product of an equilibrium constant and a rate constant.

$$\text{Olefin derivative} + F^- \underset{}{\overset{K}{\rightleftharpoons}} \text{anion}$$

$$\text{Anion} + \text{olefin derivative} \xrightarrow{k} \text{product}$$

$$\text{Overall rate} = Kk$$

While it is almost certainly the case that the equilibrium constant for forming the nitrogen anion (3) is greater than for

(2)   (1a) 65%   (1b) 16%

In a previous paper,[4] we reported that, in the presence of fluoride ion, (1a) readily forms an anion (3), which can be trapped with, for example, iodomethane. Trapping also occurs very efficiently with benzyl bromide and allyl iodide. Attempts to observe the nitrogen anion directly by n.m.r. spectroscopy are not straightforward in that rapid dimerisation to (4) occurs, using acetonitrile as solvent, but then slow reversal occurs as the solution is stirred, gradually giving a stable homogeneous solution of the anion (3). This situation obviously arises from the much lower solubility in acetonitrile of the dimer (4) compared with the monomer (1a) or anion (3). Variable temperature fluorine-19 n.m.r. studies on the anion (3) showed that little change in the spectrum occurs over a temperature range of −40 to +50 °C, indicating that reversible fluoride exchange involving anion (3) and precursor (1a) does not occur rapidly on the n.m.r. time-scale and thus the n.m.r. data truly refer to the nitrogen anion (3). Characteristically,[3,5] the resonances arising from CF_2 groups adjacent to the nitrogen anion centre are shifted *downfield* from the neutral precursors (see Experimental section) for positions adjacent to the nitrogen anion centre.

By comparison with the work on the co-oligomerisation reactions of perfluoro-cyclobutene it appeared likely that (3) could also be trapped with unsaturated fluoroalkenes and that a novel series of cyclic oligomers would result, especially since other workers have reported the fluoride ion-induced reactions
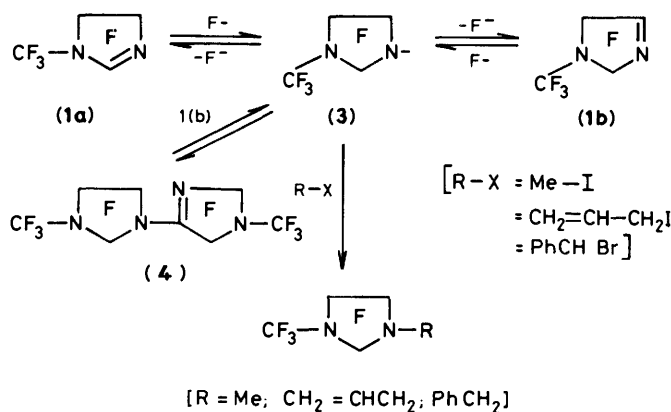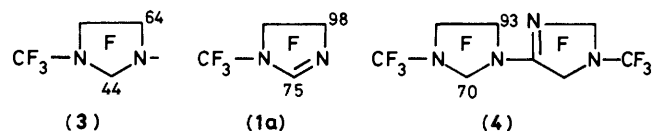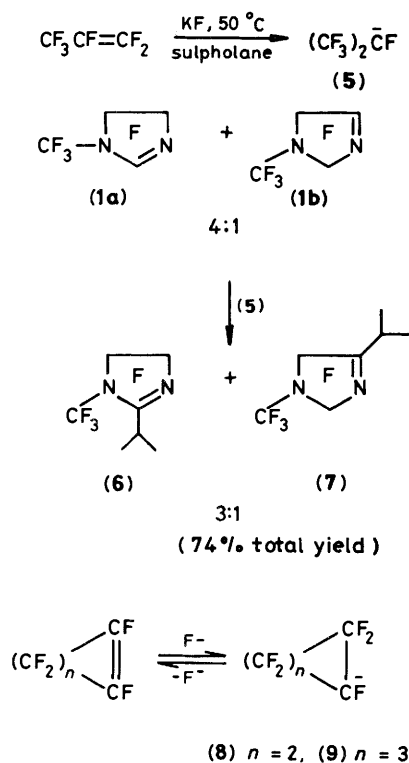

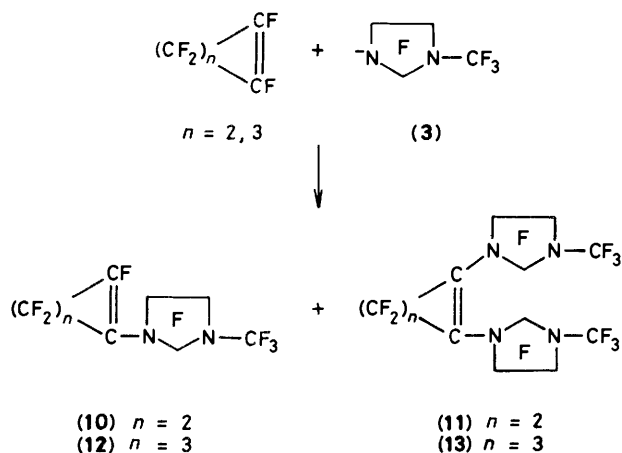δ_F Values ($CFCl_3$, positive values to highfield)

formation of the carbanion (5), the overall rate is, obviously, in favour of products derived from (5). Thus, the very stability of the nitrogen anion (3) prevents reaction with hexafluoropropene and reaction occurs *via* (5).

In contrast, reaction occurs between the anion (3) and perfluorocyclobutene and -cyclopentene, and this most probably reflects the lower equilibrium constant for forming the
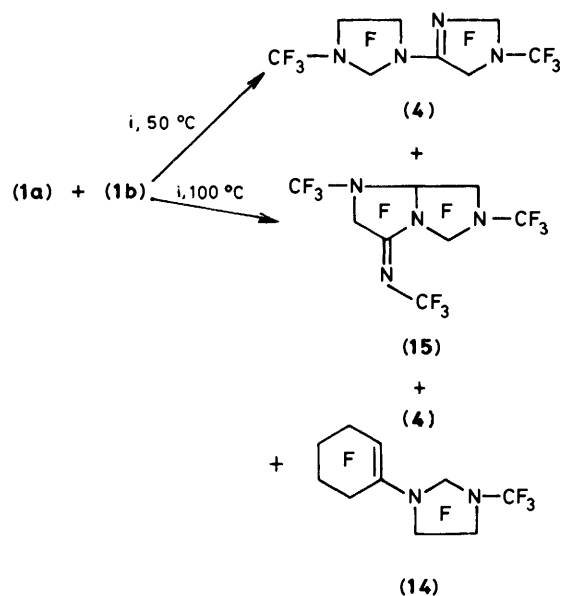
perfluoro-cyclohexene is less reactive than perfluoro-cyclopentene or -cyclobutene and we can reasonably conclude, therefore, that this lower reactivity towards nucleophiles in general accounts for the different behaviour of the nitrogen anion (3) with perfluorocyclohexene, as compared with perfluoro-cyclobutene or -cyclopentene.


Reagents: i, CsF, sulpholane, perfluorocyclohexene.

cyclic carbanions (8) and (9).[7,8] In forming these anions from the perfluorocycloalkenes, we have increased eclipsing interactions, which will be especially important in fluorinated systems.[7] Consequently, reactions of the nitrogen anion (3) now compete successfully with reactions that would involve the cyclic carbanions. By varying the ratio of the starting materials, 1:1 and 2:1 products could be isolated in high yield by preparative-scale g.l.c. and their formation can readily be described as attack of (3) on the fluoro-alkene with successive loss of fluoride ion.

Perfluorocyclohexene proved to be the least reactive olefin and a higher reaction temperature was necessary in order to give even the 1:1 product. At 50 °C the nitrogen anion (3) reacted with (1b) to give the dimer (4) in preference to reaction with perfluorocyclohexene; at 100 °C a 1:1 product (14) was, however, isolated together with dimers (4), (15), (the mechanism of formation has been discussed previously[4]), and recovered perfluorocyclohexene. It is known from other reactions that

Experimental

[19]F N.m.r. spectra were measured using a Varian EM 360L spectrometer, with trichlorofluoromethane as external reference; upfield shifts are quoted as positive. Gas chromatography was carried out using columns packed with 20% di-isodecyl phthalate on Chromosorb P (Column A) and 20% Krytox fluid on Chromosorb W (Column K). Percentage yields quoted were measured either by weighing products or by g.l.c. analysis using a gas-density balance detector. Mass spectra were recorded on a V.G. Micromass 12B linked with g.l.c.

Reactions of Perfluoro-1-methyl-1,3-diazacyclopent-2- and -3-ene (1). *With Hexafluoropropene.*—Caesium fluoride (1.0 g, 6.6 mmol) in sulpholane (5 ml) was exposed to an atmosphere of hexafluoropropene (3.8 g, 25.3 mmol) stored in a bladder and the mixture was heated to 50 °C with stirring. After *ca.* 15 min a 1:4 mixture of compounds (1a) and (1b) (1.5 g, 6.6 mmol) was injected through a septum and stirring was continued for a further 20 h. Volatile material was transferred under vacuum into a trap cooled in liquid air. The resultant liquid (3.4 g) was shown by g.l.c. (column A; room temp.) to consist of a complex mixture of liquids with six components. Separation by preparative-scale g.l.c. gave dimers and trimers of hexafluoropropene, together with *perfluoro-4-isopropyl-1-methyl-1,3-di-azacyclopent-3-ene* (7) (Found: C, 22.2; F, 70.2; N, 7.8%; M^+, 378. $C_7F_{14}N_2$ requires: C, 22.2; F, 70.4; N, 7.4%; M, 378); δ_F 60.0 (3 F, tt, J 6.5 and 5.5 Hz, F_a), 75.2 (2 F, q, J 5.5 Hz, F_b), 78.5 (6 F, dt, J 6.5 and 2.5 Hz F_d), 98.0 (2 F, br, F_e), and 196.6 (1 F, sp, J 6.5 Hz, F_c); *perfluoro-2-isopropyl-1-methyl-1,3-diazacyclopent-2-ene* (6) (Found: C, 22.3; F, 70.6; N, 7.7%; M^+, 378. $C_7F_{14}N_2$ requires C, 22.2; F, 70.4%; N, 7.4%; M, 378); δ_F 56.9 (3 F, dt, J 41.5 and 11 Hz, F_a), 77.0 (6 F, dq, J 5.5 and 2 Hz, F_c), 102.6 (2 F, s, F_d), 103.9 (2 F, q, J 11 Hz, F_e), and 189.6 (1 F, qsp, J 41.5 and 5.5 Hz, F_b).

(6)

(7)

(12)

(13)
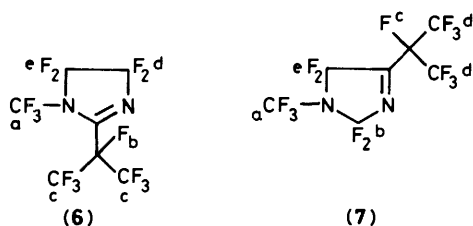
Compounds (6) and (7) were in a ratio of 3:1 and isolated in 74% total yield.

With Perfluorocyclobutene—(i) *Equimolar mixture.* A mixture containing (1) (2.28 g, 10 mmol), caesium fluoride (0.55 g, 3.6 mmol), and sulpholane (10 ml) was stirred at 50 °C for 24 h under an atmosphere of perfluorocyclobutene (1.62 g, 10 mmol). Volatile material was transferred under vacuum to a trap cooled in liquid air. After removal of recovered perfluorocyclobutene (0.52 g), the lower layer (2.50 g) was isolated and shown by g.l.c. (column K; 110 °C) to contain two components. Separation by preparative-scale g.l.c. (Column K; 100 °C) gave *perfluoro-1-(3-methylimidazolidin-1-yl)cyclobut-1-ene* (10) (26%) (Found: C, 24.65; F, 67.95; N, 7.35%; M^+, 390. $C_8F_{14}N_2$ requires C, 24.6; F, 68.2; N, 7.2%; M, 390); δ_F 58.0 (3 F, m, J 7.5 Hz, F_a), 64.7 (2 F, br s, F_b), 93.8 (4 F, br m, F_j and F_g), 117.3 (2 F, m, F_c), 119.2 (2 F, m, F_d), and 123.3 (1 F, m, F_e); and *perfluoro-1,2-bis(3-methylimidazolidin-1-yl)cyclobut-1-ene* (11) (37%), b.p. 179—181 °C (Found: C, 23.15; F, 67.3; N, 8.8%; M^+, 618. $C_{12}F_{22}N_4$ requires C, 23.3; F, 67.65; N, 9.05%; M, 618); δ_F 58.4 (6 F, F_a), 64.5 (4 F, F_b), 94.4 (4 F, F_c or F_d), 95.1 (4 F, F_c or F_d), and 116.8 (4 F, F_e).

(10)

(11)
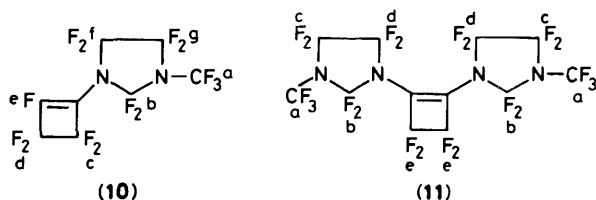
(ii) *Excess of* (1).—A mixture containing (1) (3.83 g, 16.8 mmol), caesium fluoride (0.5 g, 3.3 mmol), and sulpholane (5 ml) was stirred under an atmosphere of perfluorocyclobutene (1.35 g, 8.4 mmol) at 50 °C for 24 h. Perfluorocyclobutene (0.3 g) was recovered and preparative-scale g.l.c. (column K; 110 °C) isolated (4) (4.2%), (10) (4.2%), and (11) (65.8%).

With Perfluorocyclopentene—(i) *Equimolar mixture.* A mixture containing (1) (2.60 g, 11.0 mmol) caesium fluoride (0.56 g, 3.6 mmol), and sulpholane (10 ml) was stirred at 50 °C for 24 h under an atmosphere of perfluorocyclopentene (2.41 g, 11.0 mmol). Volatile material was transferred under vacuum into a trap cooled in liquid air. After removal of unchanged perfluorocyclopentene (1.0 g), the lower layer (2.98 g) was isolated and shown by g.l.c. (column K; 180 °C) to contain two components. Separation by preparative-scale g.l.c. (column K; 150 °C) gave *perfluoro-1-(3-methylimidazolidin-1-yl)cyclopent-1-ene* (12) (60%), b.p. 123—125 °C (Found: C, 24.55; F, 68.7; N, 6.4%; M^+, 440. $C_9F_{16}N_2$ requires C, 24.55; F, 69.1; N, 6.35%; M, 400); δ_F 59.0 (3 F, m, J 7.8 Hz, F_a), 65.0 (2 F, m, F_b), 94.0 (2 F, m, F_c), 95.8 (2 F, sp, J 2.9 Hz, F_d), 115.5 (2 F, m, F_e), 122.1 (1 F, m, F_f), 124.1 (2 F, dm, F_g), and 134.2 (2 F, m, F_h); *perfluoro-1,2-bis(3-methylimidazolidin-1-yl)cyclopent-1-ene* (13) (1%) (Found: M^+, 668. $C_{13}F_{24}N_4$ requires M, 668).

(ii) *Excess of* (1). A mixture containing (1) (4.0 g, 17.5 mmol),
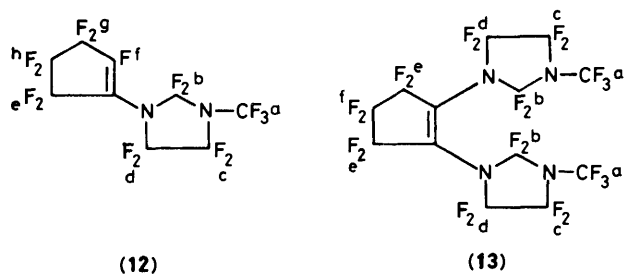
caesium fluoride (1.9 g, 6.6 mmol), and sulpholane (20 ml) was stirred at 50 °C for 18.5 h under an atmosphere of perfluorocyclopentene (2.3 g, 14.7 mmol). Volatile material was transferred under vacuum into a trap cooled in liquid air. The lower layer (5.6 g) was shown by g.l.c. (column K; 140 °C) to consist of two components. Separation by preparative-scale g.l.c. gave (12) (20%) and *perfluoro-1,2-bis(3-methylimidazolidin-1-yl)cyclopent-1-ene* (13) (16%) (Found: C, 23.09; F, 68.6; N, 8.16%; M^+, 668. $C_{13}F_{24}N$ requires C, 23.35; F, 69.25; N, 8.38%; M, 668); δ_F 58.5 (6 F, F_a), 63.9 (4 F, F_b), 93.7 (4 F, F_c or F_d), 96.0 (4 F, F_c or F_d), 115.6 (4 F, F_e), and 134.1 (2 F, F_f).

With Perfluorocyclohexene.—A mixture containing (1) (3.42 g, 15 mmol) caesium fluoride (1.0 g, 6.6 mmol), sulpholane (10 ml), and perfluorocyclohexene (1.97 g, 7.5 mmol) was heated at 100 °C for 67 h in a Carius tube. Volatile material was transferred under vacuum into a trap cooled in liquid air. The lower layer was isolated (3.90 g) and shown by g.l.c. (column K; 140 °C) to consist of five components. Separation by preparative-scale g.l.c. (column K; 150 °C and column A; 40 °C) gave unchanged perfluorocyclohexene (0.68 g), dimers (4) (1.8 g) and (15) (0.44 g), and *perfluoro-1-(3-methylimidazolidin-1-yl)cyclohex-1-ene* (14) (26%) b.p. 143—145 °C (Found: C, 24.35; F,

(14)
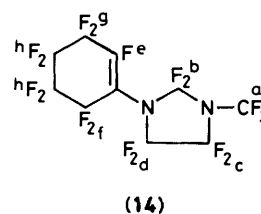
70.1; N, 6.05%; M^+, 490. $C_{10}F_{18}N_2$ requires C, 24.5; F, 69.8, N, 5.7%; M, 490); δ_F 58.3 (6 F, m, J 8 Hz, F_a), 64.3 (2 F, br, F_b), 92.5 (2 F, br, F_c), 94.1 (2 F, br, F_d), 112.6 (1 F, br m, F_e), 113.6 (2 F, br, F_f), 121.9 (2 F, d, J 21.6 Hz, F_g), and 135.5 (4 F, F_h).

A similar reaction at 50 °C gave only dimer (4) and perfluorocyclohexene.

With Benzyl Bromide.—A mixture containing (1) (1.43 g, 6.72 mmol), caesium fluoride (1.56 g, 10.26 mmol), and benzyl bromide (1.05 g, 6.14 mmol) in acetonitrile (3 ml) was stirred at room temperature for 41 h. Volatile material was transferred under vacuum to a trap cooled in liquid air. G.l.c. (column K, 150 °C) showed only one product. A sample was separated from the solvent by preparative-scale g.l.c. (column K, 150 °C) and shown to be 1-*benzyl-2,2,4,4,5,5-hexafluoro-3-trifluoromethyl-1,3-diazacyclopentane* (Found: C, 39.1; H, 1.7; N, 8.1%; M^+, 338. $C_{11}H_7F_9N_2$ requires C, 39.0; H, 2.1; N, 8.3%. M, 338); δ_F 56.00 (3
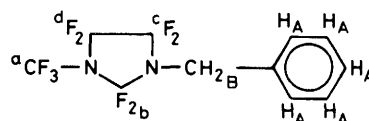
F, p, *J* 7.29 Hz, F$_a$), 64.67 (2 F, m, *J* 7.53 Hz, F$_b$), 91.83 (2 F, t, *J* 8.00 Hz, F$_c$), and 93.00 (2 F, m, 6.59 Hz, F$_d$); δ_H 4.4 (2 H, br s, H$_B$), and 7.4 (5 H, br s, H$_A$).

With Allyl Iodide.—A mixture containing (1) (7.71 g, 33.82 mmol), caesium fluoride (7.00 g, 46.05 mmol), and allyl iodide (5.68 g, 33.80 mmol) in sulpholane (15 ml) was stirred at 30 °C for 6 h. Volatile material (9.60 g, 98.6%) was transferred under vacuum to a trap cooled in liquid air. G.l.c. (column K, 90 °C) showed it to be pure product, identified as 1-*allyl*-2,2,4,4,5,5-*hexafluoro*-3-*trifluoromethyl*-1,3-*diazacyclopentane* (Found: C, 29.4; H, 2.1; N, 9.9%; *M*$^+$, 228. C$_7$H$_5$F$_9$N$_2$ requires C, 29.2; H, 1.7; N, 9.7%; *M*, 228); δ_F 59.5 (3 F, p, *J* 7.29 Hz, F$_a$), 68.67 (2 F, m, *J* 7.53 Hz, F$_b$), 97.0 (4 F, br m, F$_c$); δ_H 4.05 (2 H, br d, 5.6 Hz, H$_A$), 5.45 (1 H, br m, H$_B$), 5.65 (1 H, br s, H$_C$), and 5.95 (1 H, m, H$_D$).
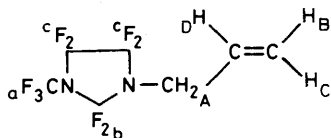
With Caesium Fluoride.—A mixture containing (1) (0.18 g, 0.79 mmol) caesium fluoride (0.52 g, 3.42 mmol), and [^{2}H$_3$]acetonitrile (1 ml) was stirred at ambient temperature for *ca.* 30 s. The ^{19}F n.m.r. spectrum of the mixture showed only dimer (4). However, after the mixture had been stirred for a further 72 h a pale yellow colour was observed, and the ^{19}F n.m.r. spectrum of the mixture showed only the perfluoro-3-methyl-1,3-diazacyclopentane anion (3); δ_F 58.3 (3 F, br, F$_a$), 44.0 (2 F, br, F$_b$), 64.8 (2 F, br, F$_c$), and 94.1 (2 F, br, F$_d$). Variable-temperature studies on the solution containing (3) showed no significant changes between 233 and 323 K.

(3)
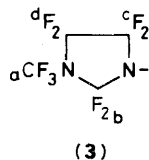
Addition of a drop of bromine to a sample in the n.m.r. tube caused the spectrum to collapse instantly showing a mixture of the dimer (4) and another compound, probably 1-bromo-2,2,4,4,5,5-hexafluoro-3-trifluoromethyl-1,3-diazacyclopentane; δ_F 58.0 (3 F, p, *J* 7.53 Hz, F$_a$), 58.8 (2 F, br, F$_b$), 84.5 (2 F, br, F$_c$), and 94.0 (2 F, br, F$_d$).
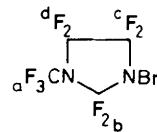
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