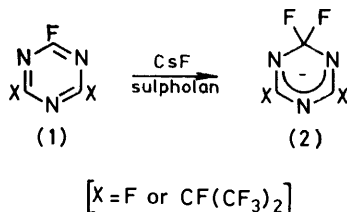


## Reactions involving Fluoride Ion. Part 19.<sup>1</sup> Observable Perfluorocycloalkyanions

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Carbanions are generated by reaction of fluoride ion with perfluorocycloalkene derivatives, *e.g.* perfluorobicyclobutylidene (3), and this anion is relatively unchanged over a range of temperature or on prolonged standing, as indicated by the <sup>19</sup>F n.m.r. spectrum. Internal return by fluoride ion to the same carbon atom is suggested to account for the <sup>19</sup>F n.m.r. spectra of the ions. Trapping experiments with bromine and chlorine provide further evidence for the structures of the ions.

In this series we have been relating the role of fluoride ion, in reactions with unsaturated fluorocarbons, with the role of the proton, in reactions with unsaturated hydrocarbons, and one of the attractive objectives in this area is to generate long-lived, *observable* carbanions *via* fluoride ion. We have achieved this in one earlier case, *i.e.* the generation of  $\sigma$ -complexes (2) from triazines (1)<sup>2</sup> and other workers have generated  $\sigma$ -complexes by adding fluoride ion to trinitrobenzene<sup>3</sup> and the fluoro-derivative.<sup>4</sup> The generation of carbanions by addition



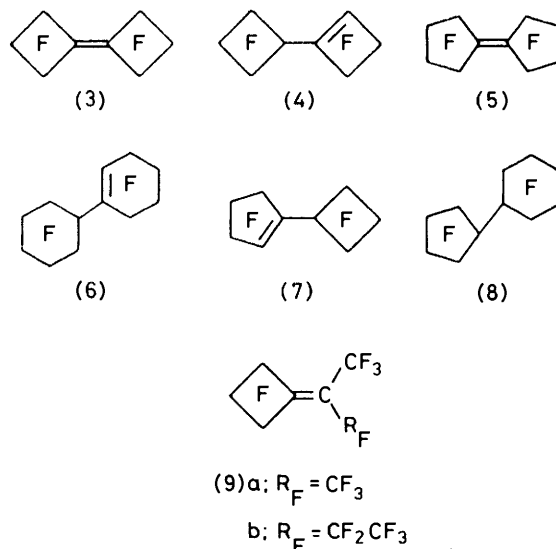
of fluoride ion to a variety of fluoro-olefins and to hexafluorobut-2-yne has been demonstrated, in a now considerable literature on reactions of these species.<sup>5-7</sup> In one case<sup>8</sup> there is clear evidence that a long-lived ion is produced but direct observation by spectroscopy is not reported.

In earlier publications<sup>1,9,10</sup> we have described the syntheses of some novel fluoro-cycloalkene derivatives (3)–(9). Formally, (3) is closely related to perfluoro-3,4-dimethylhex-3-ene (10).<sup>11-13</sup> However, we are finding<sup>14</sup> that (3) is of considerably greater reactivity than (10) and this may be attributed to the activating effects of angle strain. We have demonstrated<sup>13,15</sup> that, in the presence of fluoride ion, (10) is in equilibrium with its isomers (10a and b) but there is no evidence of any significant concentration of the anion (11) in solution, *e.g.* caesium fluoride does not dissolve in a mixture of (10) and dimethylformamide, nor is the <sup>19</sup>F n.m.r. spectrum of (10) changed by interaction with this system.

In complete contrast, we have observed that caesium fluoride dissolves in a mixture of (3) and dimethylformamide, and this is especially dramatic because, individually, neither caesium fluoride nor (3) is significantly soluble in this solvent. We attribute the formation of this solution to generation of the ion (12) and we have shown that (12) may be trapped with bromine giving the

corresponding bromo-derivative (13), with no detectable reversion to the starting material (3),(4).

More significantly, the ion (12) is now directly observable by <sup>19</sup>F n.m.r. Signals were observed for two non-equivalent ring systems (see Figure) and there was no evidence for the presence of the dimers (3),(4). The induced asymmetry of the system rules out the possibility of rapid intermolecular exchange of fluoride ion and this is supported by the observation that essentially only one molecular proportion of caesium fluoride dissolves for each molecular proportion of (3),(4). This fact was determined by filtration of the solution of (12), followed by removal of volatile material by heating under vacuum, leaving only caesium fluoride. Also, the fact that the

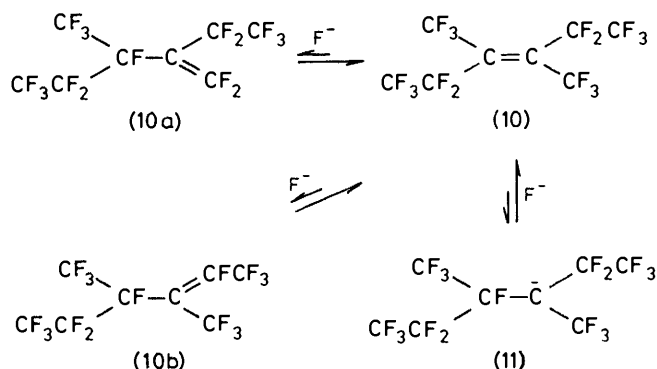


A fluorine symbol within a ring signifies that all unmarked positions in that ring are bonds to fluorine

spectrum remains relatively unchanged over a very significant temperature range, *i.e.* –80 to +100 °C, confirms this and we can conclude, therefore, that the system is wholly in the form of the anion (12), within the limits of detection.

There are, however, two puzzling features of the spectrum of the ion (12) and other ions described later that we are unable to explain. First, we have been unable to

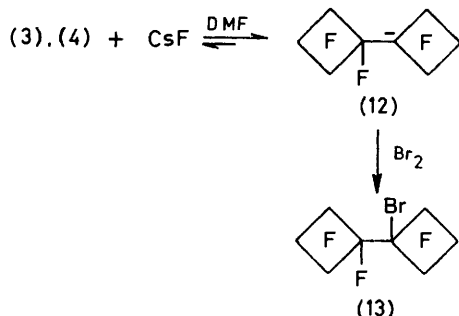
observe a resonance corresponding to the added tertiary fluorine atom in the anion (12). We have ruled out intermolecular exchange of fluoride ion but there is the possibility that a degree of dissociation of the anion (12) occurs but with rapid internal-return to the same carbon atom. This would maintain the asymmetry of the



system but could lead to extensive broadening of the resonance associated with the tertiary fluorine atom.

A second puzzling feature of the  $^{19}\text{F}$  n.m.r. spectrum of anion (12) is the fact that the resonance corresponding to difluoromethylene groups adjacent to the charged centre occurs significantly *downfield* of the corresponding resonance in a saturated four-membered ring, e.g. in compound (4). This is paralleled by the C-13 n.m.r. spectrum of (12) although here the carbon bearing the negative charge is apparently shifted *upfield*, which corresponds with other carbanions that have been studied.<sup>16</sup> Other anions, described later, all show this low-field shift for difluoromethylene groups adjacent to a carbanion centre but, at the present time, we are unable to advance a satisfactory explanation of this effect.

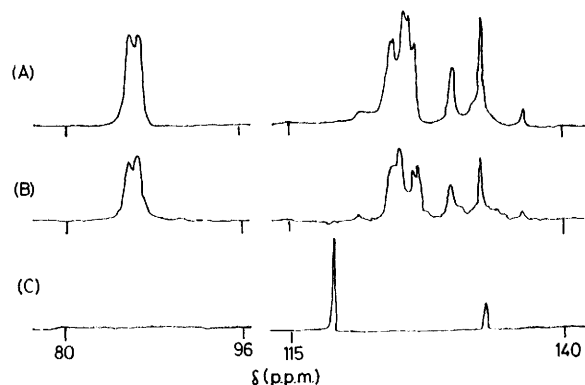
The  $^{19}\text{F}$  n.m.r. spectrum of (12) was relatively unaffected by a change from the use of caesium fluoride to



potassium fluoride, with or without added 18-crown-6-polyether. However, the potassium salt of the anion (12) was less thermally stable; as the temperature was raised above *ca.* 45 °C, some broadening of the spectrum occurred and this was accompanied by precipitation of potassium fluoride and the fluorocarbon (3),(4). This is, of course, quite consistent with the well-known fact that caesium fluoride is a better fluoride-ion donor than potassium fluoride. A closely similar spectrum of (12)

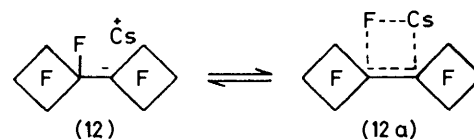
was also obtained when the ion was generated in tetraglyme as solvent.

We have examined reactions of caesium fluoride with other compounds related to (3) and obtained similar evidence for the formation of a number of long-lived fluoro-carbanions. Compounds (9a) and (9b) each gave a single anion (14a) and (14b) which, on quenching with bromine gave the corresponding bromo-derivatives (15a) and (15b). This indicates that the anions had the structures (14) and furthermore, the  $^{19}\text{F}$  n.m.r. spectra corresponded with (14) rather than the alternative ions (16). Again, however, in the  $^{19}\text{F}$  n.m.r. spectra of the ions (14) we were unable to find a resonance corresponding to a tertiary fluorine atom. The fact that the charge



$^{19}\text{F}$  N.m.r. spectra of perfluorobicyclobutylidene (3),(4): (C) at +40 °C, (A) and (B) with added caesium fluoride at -60 and +40 °C respectively

is exclusively located on the 4-membered ring is, of course, consistent with the electronegativity of a carbon atom in such a ring but the formation of the alternative anions (16) would also be inhibited by increasing eclipsing interactions in the ring. That eclipsing interactions would be important in ions (16) is confirmed by the fact that two anions (17) and (18) are observed from (7) and, correspondingly, *two* bromo-derivatives (19) and (20) are obtained on quenching. Furthermore, the relative



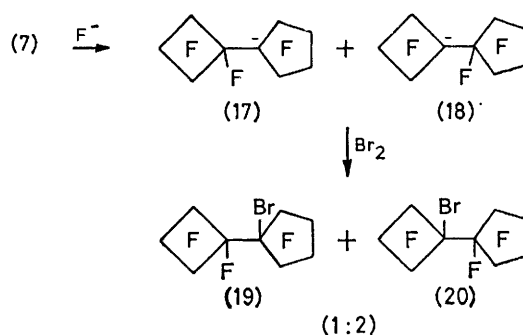
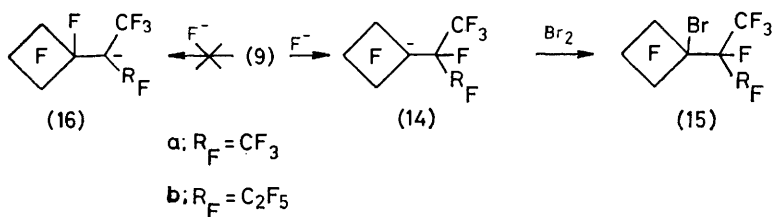
proportions of the bromo-derivatives (19) and (20) are in the same order as the relative proportions of the anions (17) and (18) in solution, as estimated by n.m.r. The additional eclipsing interactions associated with adding fluoride ion to the four- or five-membered rings in (7) would be reasonably similar and this accounts for the formation of *two* ions (17) and (18), although the latter was in excess. This idea of unavoidable extra eclipsing interactions, associated with the ions (17) and (18) in comparison with (14a and b) accounts for the fact that (17) and (18) are much less stable. As the temperature is raised the signals for (17) and (18) in the  $^{19}\text{F}$  n.m.r. spectrum rapidly broaden and, at 80 °C, a *single sharp*

resonance is observed. The rapid averaging of the fluorine atoms indicates a remarkably fast series of  $S_N2'$  processes, some of which are illustrated.

The much less strained compound (5) does not dissolve in the caesium fluoride–dimethylformamide system and, therefore, (5) behaved like the acyclic olefin (10). Clearly the strain in (5) is an insufficient driving force to

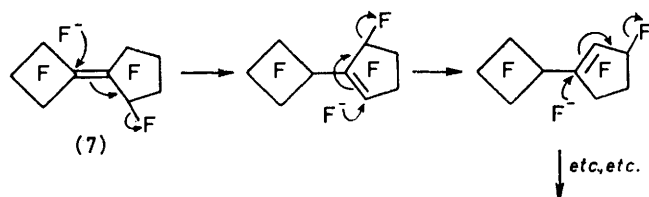
and the other *endo* isomers will be destabilised by vinylic fluorine atoms.<sup>17</sup>

In this paper we have demonstrated that *observable* anions can be generated in a simple fluoride-induced process and the special features of these systems are that they are very stable tertiary anions and, furthermore, once produced are relatively crowded. Hence further

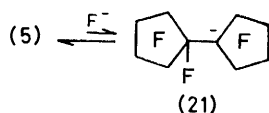


overcome eclipsing interactions that would be introduced by forming anion (21).

The endocyclic compounds (6) and (8) form anions readily. However, although the  $^{19}F$  n.m.r. spectra

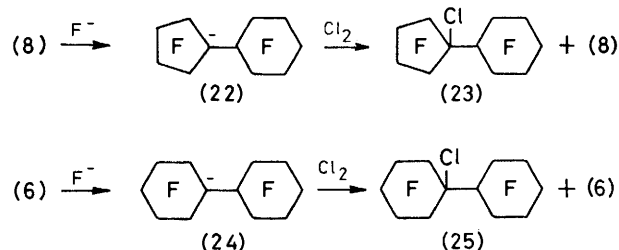


clearly indicate that these anions are fully formed, they could not be satisfactorily quenched with bromine. In contrast, quenching with chlorine proceeded rapidly to give the chloro-derivatives (25) and (23) respectively. The low reactivity of anions (22) and (24) towards bromine is presumably due to steric crowding at the anionic site in each of these anions. The fact that the



anion (22) is formed readily whereas (21) is not, at first sight appears contradictory. It seems unlikely that the difference between these two systems lies in the anions (21) and (22), but rather in the initial state energies of the corresponding cycloalkenes (5) and (8), since (8)

reaction of anion with starting material is therefore inhibited.



#### EXPERIMENTAL

Caesium fluoride was dried by heating under vacuum with frequent agitation and periodic grinding in a glove-bag followed by storage under dry nitrogen. Potassium fluoride was dried by strong heating in air followed by grinding and then heating under high vacuum. Dimethylformamide (DMF) was redistilled at reduced pressure under nitrogen; the middle fraction was collected and stored, under nitrogen, over 4A molecular sieve.

$^{19}F$  N.m.r. spectra were recorded using a Varian 56/60D spectrometer; fluorotrichloromethane was used as external standard and *upfield* shifts (p.p.m.) are recorded as positive.  $^{13}C$  N.m.r. spectra were recorded using a JEOL 100-MHz spectrometer; tetramethylsilane was used as external standard and *downfield* shifts (p.p.m.) are recorded as positive. G.l.c. was carried out using a Varian Aerograph instrument fitted with a gas density balance detector. Two columns were used: column O, 30% silicone SE30 on Chromosorb G60–80; and column Z, 2-cyanomethyl-

silicone on Chromosorb P. Mass spectra were recorded using an A.E.I. MS9 spectrometer or a VG Micromass 12B spectrometer linked with a gas chromatograph. I.r. spectra were recorded using a Perkin-Elmer 577 spectrophotometer. Boiling points were measured by the Siwoloff method.

*Direct Observation and Trapping of Fluorocarbanions.*—*General procedure.* Unless otherwise stated, all reactions were carried out using the following procedure. The fluorocarbon was stirred at room temperature with an excess of caesium fluoride in DMF as solvent until a homogeneous solution was obtained. Stirring was then discontinued and the mixture allowed to stand for *ca.* 30 min. A small sample of liquid was then removed and a  $^{19}\text{F}$  n.m.r. spectrum recorded. To the residue was added an equimolar amount of bromine and the resulting mixture was stirred for *ca.* 1 h. Volatile material was transferred, under vacuum, to a cold-trap and then poured into water; the lower fluorocarbon layer was removed, washed with water, dried ( $\text{P}_2\text{O}_5$ ), and transferred to a cold-trap under vacuum.

*Reaction of Compounds (3) and (4).*—A mixture of caesium fluoride (4.5 g, 29.6 mmol), compounds (3) and (4) (3.4 g, 10.5 mmol), and DMF (20 ml) was quenched with bromine (1.7 g, 10.6 mmol). The product (4.0 g) was shown by g.l.c. (column O) to be a single compound subsequently identified as 1-bromoperfluoro-1-cyclobutylcyclobutane (13) (90%) [Found: C, 22.5; F, 58.6; Br, 19.6%;  $M^+$  424 ( $^{81}\text{Br}$ ).  $\text{C}_8\text{F}_{13}\text{Br}$  requires C, 22.70; F, 58.41; Br, 18.89%;  $M$ , 424 ( $^{81}\text{Br}$ )], b.p. 125 °C, i.r.  $\lambda_{\text{max}}$  7.24, 7.81, 8.20, 9.95, and 10.05  $\mu\text{m}$ ;  $\delta_{\text{F}}$  168.3 (1 F, m,  $J$  14 Hz,  $\text{>CF}$ ), 131.1 (2 F, in fully fluorinated ring), 126.3 (4 F, m, in fully fluorinated ring), 125.5 and 130.7 (2 F, AB,  $J$  223 Hz), and 108.4 and 122.1 (4 F, AB,  $J$  220 Hz). These assignments are made possible because the influence of bromine on the  $^{19}\text{F}$  n.m.r. spectrum is apparent from the fact that signals arising from adjacent  $\text{CF}_2$  groups are significantly affected. One half of each AB signal is broadened (presumably, corresponding to the fluorine atoms that are *cis* to the bromine atom) and moved to lower field than *e.g.* the signals arising from compound (4).

The anion (12) showed  $\delta_{\text{F}}$  86.6 (4 F, d,  $J$  52 Hz, F atoms adjacent to anionic centre) and signals between 119 and 137 (8 F, unassigned); the  $^{19}\text{F}$  n.m.r. spectra obtained using potassium as the counter-ion and caesium as the counter-ion in different solvents, *i.e.* tetraglyme, tetraglyme-DMF, acetonitrile-DMF, were essentially identical with that reported above;  $\delta_{\text{C}}$  52.2 (1C, anionic centre), 96.3 (1 C), 112.9 (2 C), 113.8 (1 C), 116.7 (1 C), and 128.9 (2 C).

*Reaction of Compound (9a).*—A mixture of caesium fluoride (1.24 g, 8.16 mmol), compound (9a) (0.72 g, 2.31 mmol), and DMF (5 ml) was quenched with bromine (0.43 g, 2.69 mmol). The product (0.86 g) was shown by g.l.c. (column O) to consist of one major component and several minor unidentified ones. The major component (0.54 g) was separated by preparative g.l.c. and subsequently identified as 1-bromoperfluoro-1-isopropylcyclobutane (15a) (57%) [Found: C, 20.2; Br, 20.1; F, 59.5%;  $M^+$  412 ( $^{81}\text{Br}$ ).  $\text{C}_7\text{F}_{13}\text{Br}$  requires C, 20.44; Br, 19.46; F, 60.10%;  $M$ , 412 ( $^{81}\text{Br}$ )], b.p. 110 °C, i.r.  $\lambda_{\text{max}}$  7.14, 7.69, 7.94, 8.01, 8.22, 8.47, 8.86, 9.95, 12.36, 13.35, and 14.04  $\mu\text{m}$ ;  $\delta_{\text{F}}$  72.3 (6 F, m,  $\text{CF}_3$ ), 112.1 and 124.6 (4 F, AB,  $J$  220 Hz, cyclobutyl ring), 124.3 and 128.6 (2 F, AB,  $J$  220 Hz), and 171.6 (1 F, t,  $J$  54 Hz,  $\text{>CF}$ ). The anion (14a) showed  $\delta_{\text{F}}$  74.4 (6 F), 88.6 (4 F), and 125.3 (2 F).

*Reaction of Compound (9b).*—A mixture of caesium

fluoride (3.07 g, 20.2 mmol), compound (9b) (2.08 g, 5.75 mmol), and DMF (10 ml) was quenched with bromine (1.17 g, 7.31 mmol). The product (2.46 g) was shown by g.l.c. to contain a mixture of (9b) (*ca.* 10%) and one other component which was separated by preparative g.l.c. and identified as 1-bromoperfluoro-1-isobutylcyclobutane (15b) (1.54 g, 58%) [Found: C, 21.1; F, 62.8; Br, 16.7%;  $M^+$  462 ( $^{81}\text{Br}$ ).  $\text{C}_8\text{F}_{15}\text{Br}$  requires C, 20.8; F, 61.8; Br, 17.4%;  $M$ , 462 ( $^{81}\text{Br}$ )], i.r.  $\lambda_{\text{max}}$  7.15, 7.49, 7.84, 8.10, 8.33, 8.47, 9.20, 9.91, and 13.50  $\mu\text{m}$ ;  $\delta_{\text{F}}$  71.3 (3 F, m), 82.5 (3 F, m,  $\text{CF}_2\text{CF}_3$ ), 113.0 (2 F, m,  $\text{CF}_2\text{CF}_3$ ), 112.1 and 125.7 (4 F, AB,  $J$  *ca.* 216 Hz,  $\text{CF}_2$  in a cyclobutyl ring), 125.3 and 129.7 (2 F, AB,  $J$  224 Hz,  $\text{CF}_2$  in a cyclobutyl ring), and 170.6 (1 F, m,  $\text{>CF}$ ). The anion (14b) showed  $\delta_{\text{F}}$  74.6 (3 F), 81.2 (3 F,  $\text{CF}_2\text{CF}_3$ ), 88.6 (4 F), 118.5 (2 F,  $\text{CF}_2\text{CF}_3$ ), and 126.1 (2 F,  $\text{CF}_2$  in a cyclobutyl ring).

*Reaction of Compound (7).*—A mixture of caesium fluoride (2.00 g, 13.16 mmol), compound (7) (2.50 g, 6.68 mmol), and DMF (10 ml) was quenched with bromine (1.07 g, 6.69 mmol). The product (2.75 g) was shown by g.l.c. (column O) to be a mixture containing compound (7) (*ca.* 10%), one other major component, and three minor unidentified products. A sample (2.47 g) was purified by preparative g.l.c. and the major component (1.49 g, 52%) shown by  $^{19}\text{F}$  n.m.r. and g.l.c.-ms (column Z) to be a mixture (*ca.* 2 : 1) of 1-bromoperfluoro-1-cyclopentylcyclobutane (20) and 1-bromoperfluoro-1-cyclobutylcyclopentane (19) [Found: C, 23.1; F, 59.4; Br, 17.7%;  $M^+$ , 474 ( $^{81}\text{Br}$ ).  $\text{C}_9\text{F}_{15}\text{Br}$  requires C, 22.83; F, 60.25; Br, 16.91%;  $M$ , 474 ( $^{81}\text{Br}$ )]. Assignment of (20) as the major isomer follows from identification of the strongest resonance in the  $^{19}\text{F}$  n.m.r. spectrum ( $\delta$  135.1, s), as resulting from the fluorine atoms attached to C-1 and -4 in a saturated perfluorocyclopentyl ring.

The anions (17) and (18) showed  $\delta_{\text{F}}$  (20 °C) 81.8 [4 F, in anion (17),  $-\text{CF}_2-$  adjacent to anionic site], 89.4 [4 F, in anion (18),  $-\text{CF}_2-$  adjacent to anionic site], and signals between 117 and 138 (unassigned). From integration the ratio of (18) : (17) is approximately 4 : 1 respectively; at 80 °C only one signal, at  $\delta$  127.7, is observed. The assignment of the  $\delta$  89.4 signal to the anion (18) follows simply by comparison of spectra with those of other anions, described earlier, where the negative charge is situated on a fluorinated cyclobutyl ring.

*Reaction of Compound (6).*—A mixture of caesium fluoride (2.7 g, 17.8 mmol), compound (6) (1.43 g, 2.73 mmol), and DMF (15 ml) was stirred for 1 h at room temperature. A small sample of the resultant solution was removed and its  $^{19}\text{F}$  n.m.r. spectrum recorded at various temperatures. These indicated the presence of anion (24) in solution,  $\delta_{\text{F}}$  75.8 ( $\text{CF}_2$  adjacent to anionic site) and signals between 115 and 143 (unassigned).

Chlorine (*ca.* 1.4 g) was bubbled through the residue and the resultant solution stirred until it had cooled to room temperature. Volatile material was then transferred, under vacuum, to a cold-trap and filtered, to give a white solid (1.22 g). This was shown by g.l.c. (etheral solution) to be a single compound containing traces of DMF. A sample was purified by dissolving in ether, washing with water, drying ( $\text{MgSO}_4$ ), and removal of the ether. The resultant solid was identified as 1-chloroperfluoro-1-cyclohexylcyclohexane (25) (77%), m.p. 80–81 °C [Found: C, 24.9; F, 68.6; Cl, 6.6%;  $M^+$ , not observed, highest peak at  $m/e$  559 ( $^{35}\text{Cl}$ ,  $M^+ - 19$ ).  $\text{C}_{12}\text{F}_{21}\text{Cl}$  requires C, 24.89; F, 68.97; Cl, 6.14%;  $M$ , 578 ( $^{35}\text{Cl}$ )]; i.r.  $\lambda_{\text{max}}$  8.08, 8.26, 8.44, 8.65, 9.65, 10.56, 10.73, and 10.88  $\mu\text{m}$ ;  $\delta_{\text{F}}$  166.0

(1 F, br s,  $\geq$ CF) and signals between 101 and 149 (20 F) (unassigned).

*Reaction of Compound (8).*—The procedure was as for compound (6). Thus, a mixture of caesium fluoride (2.1 g, 13.8 mmol), compound (8) (1.30 g, 2.74 mmol), and DMF (10 ml) gave the anion (22) in solution,  $\delta_F$  79.0 (CF<sub>2</sub>, adjacent to anionic site) and signals between 110 and 145 (unassigned).

Quenching with chlorine gave a white solid (1.06 g), identified as 1-chloroperfluoro-1-cyclohexylcyclopentane (23) (73%): m.p. 45 °C [Found: C, 24.8; F, 68.8; Cl, 6.6%;  $M^+$ , 528 (<sup>35</sup>Cl; very weak). C<sub>11</sub>F<sub>19</sub>Cl requires C, 24.98; F, 68.31; Cl, 6.72%;  $M$ , 528 (<sup>35</sup>Cl)]; i.r.  $\lambda_{\max}$  7.51, 7.62, 7.69, 7.89, 8.01, 8.12, 8.20, 8.28, 8.35, 8.70, 9.53, 9.73, 9.87, and 10.62  $\mu$ m;  $\delta_F$  174.6 (1 F, br m,  $\geq$ CF) and signals between 101 and 149 (18 F) (unassigned).

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