

Reactions Involving Fluoride Ion. Part 25.¹ A Fluoride-ion-induced Skeletal Rearrangement²

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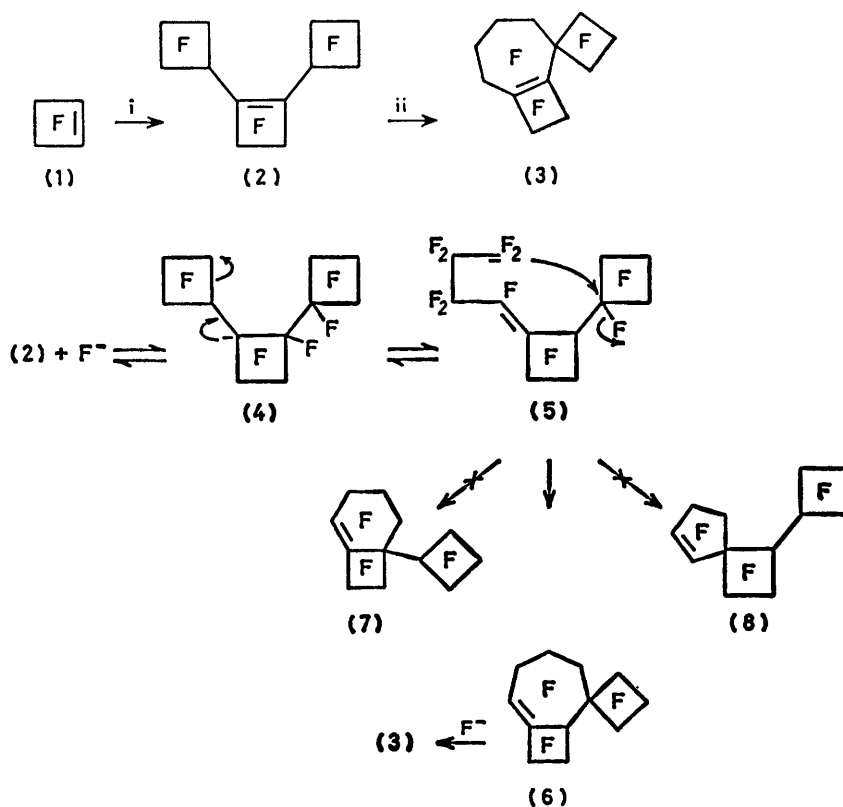
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Reaction of a perfluorocyclobutene trimer (2) with fluoride ion at room temperature gives a remarkable rearrangement to a seven-membered-ring compound (3). This cyclisation is formulated as an intramolecular displacement of fluoride, from a saturated site. The structure of (3) follows partly from pyrolysis studies, giving a series of seven-membered-ring compounds (21)—(23) derived from (3) by loss of C_2F_4 and isomerisation.

IN previous parts of this series, we have been pursuing studies into the analogy between the role of fluoride ion, in reactions with unsaturated fluorine-containing compounds, and the proton in its well known reactions with unsaturated hydrocarbons. So far, the analogy includes³ fluoride-ion-induced (i) oligomerisations of fluorinated olefins, (ii) 'negative Friedel-Crafts' reactions, (iii) rearrangements of perfluoroalkylaromatic compounds, and, more recently, (iv) formation of observable anionic σ -complexes⁴ and carbanions.⁵ This analogy between proton- and fluoride-ion-induced processes has covered a remarkable range of reactions, but we are comparing, in effect, carbocation chemistry with fluorinated carbanion chemistry and, consequently, we

would not expect an extension of the analogy to include saturated fluorinated carbanions. Nevertheless, we report here a remarkable rearrangement that involves a saturated fluorinated carbanion.

We have previously described an interesting range of oligomers obtained from perfluorocyclobutene (1), using fluoride ion or pyridine.⁶ We now find that the trimer (2), obtained from (1) with pyridine at room temperature, undergoes a surprisingly rapid rearrangement in the presence of caesium fluoride in dimethylformamide (DMF), at room temperature, giving a high yield of a single product (3), the structure of which follows from a combination of spectral data and further reactions, which are described later.



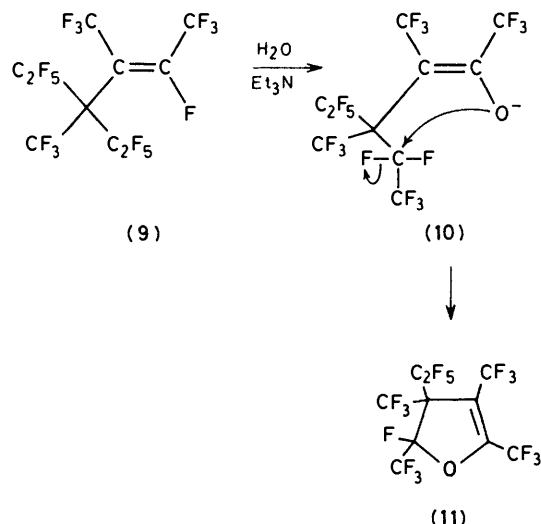
SCHEME 1 Reagents: i, pyridine; ii, CsF, DMF, room temperature. (The presence of F within a ring signifies that all unmarked positions in that ring are attached to fluorine.)

A mechanism to account for the formation of (3) is given in Scheme 1, which incorporates addition of fluoride ion to (2) and then ring-opening of the resultant anion (4). There is, of course, ample precedent elsewhere for ring-opening of cyclobutylmethyl anions.⁷ In this case, in addition to relief of angle-strain, ring opening of (4) would also be assisted by relief of eclipsing interactions by introducing an unsaturated site into a remaining four-membered ring, *i.e.* (5), since eclipsing interactions seem to be especially important with fluorinated compounds.⁵ Compound (6) is not observed, but simple allylic displacement by fluoride ion would lead to (3). The step (5) → (6) involves intramolecular nucleophilic displacement of fluorine from a saturated site and, until recently, there was no precedent for this process. We did, however, describe⁸ the cyclisation of (9) to (11), *via* the anion (10), and this cyclisation can only be rationalised as shown. Other workers⁹ have cast doubt on the structure of (11), and the associated mechanism, but the position of resonance of the 'tertiary' fluorine atom⁸ in the ¹⁹F n.m.r. spectrum of (11) is definitive.¹⁰

We cannot be similarly definitive about the mechanism of formation of (6) and (3) since an alternative approach is, in principle, possible; this is outlined in Scheme 2. Here the key process would be rearrangement of the double bond in (5), eventually giving (14), and then the cyclisation step would be the more conventional nucleophilic addition to an unsaturated site, with allylic displacement of fluorine, (14) → (3). If, however, the ion (5) has any prolonged lifetime, we would anticipate elimination of fluoride ion giving (15), and then re-addition to give the more stable anion (16), but no products arising from (16) have been observed. The instability of primary perfluoroalkyl anions is well

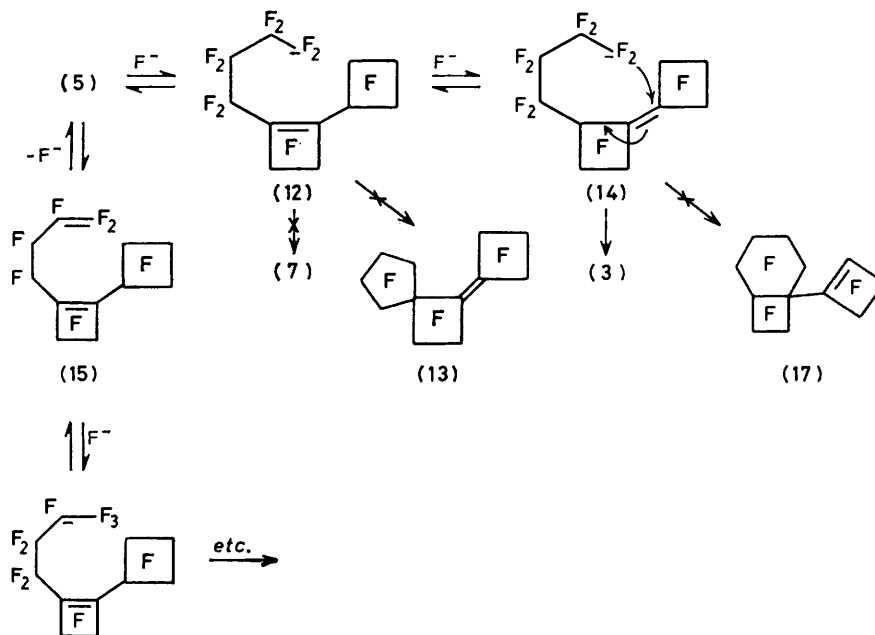
documented.¹¹ Overall, therefore, we prefer Scheme 1 to Scheme 2.

The formation of a seven-membered ring (3) exclusively, and easily, is surprising when the alternative of formation of five- or six-membered rings seems to be available, *i.e.* forming compounds (7), (8), or (13), but



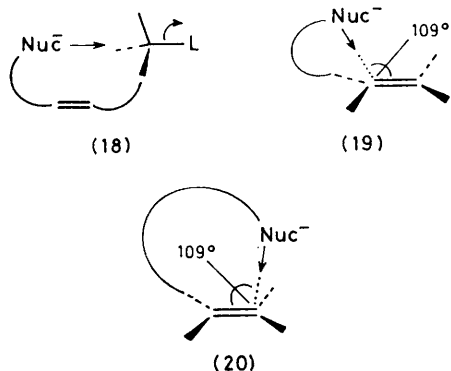
none of these was detected in the product. This complete selectivity is more understandable through inspection of models and by consideration of the 'Baldwin Rules'¹² for nucleophilic ring-closure reactions. The favourable stereochemistry for attack at a tetrahedral site is (18) and for *exo*- or *endo*-ring closure at a trigonal site, (19) or (20), respectively.

Models indicate that the conversion of (5) into (6) can



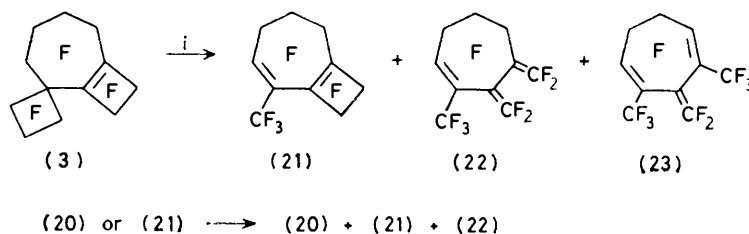
SCHEME 2

be achieved with an ideal arrangement of groups (18) in the transition state for a nucleophilic displacement of fluorine. In contrast, it is not possible to adopt an ideal approach (18) for the conversion of (5) into (7). Likewise, models showed that ring closure of (5) into (8) cannot achieve the favourable approach (20). In contrast, however, if we consider the process described in



Scheme 2 then there is great difficulty in explaining the selective formation of (3) rather than (13), (7), or (17). Models show that conversion of (12) into (7) would be difficult, since the approach (20) could not be adopted, but the conversions (12) \rightarrow (13) or (14) \rightarrow (17), both through (19), are examples of highly favourable closure processes.¹² Therefore, overall, the observations seem to be most adequately explained by the unusual and controversial mechanism contained in Scheme 1.

Proof of the structure of (3) comes from a variety of data. The ¹⁹F n.m.r. spectrum shows only signals corresponding to CF₂ groups, including two AB quartets that are typical of a perfluorocyclobutane ring. The i.r. spectrum shows a weak absorption at 1 678 cm⁻¹ (C=C stretch), typical of (R_F)₂C=C(R_F)₂ (R_F = perfluoroalkyl).¹³ Further substantial proof of structure of (3)



SCHEME 3 i, 590 °C, Pt tube, flow system in N₂

comes, however, from pyrolysis experiments, the results of which are shown in Scheme 3.

Compound (3) was carried in a stream of dry nitrogen through a Pt-lined tube at 590 °C; the product contained compounds (21)—(23). Samples of each were separated by preparative-scale g.l.c. and were shown by elemental analysis and mass spectrometry to be isomers of C₁₀F₁₄. Furthermore, on re-circulation of separate samples (21) and (22) through the pyrolysis tube each gave comparable product mixtures containing (21)—(23).

The structure of compound (23) followed simply from the ¹⁹F n.m.r. spectrum; the symmetrical structure showed only resonances corresponding to -CF₂⁻, -CF₃, and =CF₂ groups, with the appropriate intensities. There are two symmetrical structures possible but only (23) is compatible with the conversions shown in Scheme 3. Structural features contained in compounds (21) and (22) also follow easily from the ¹⁹F n.m.r. spectra, but again only isomers (21) and (22) are compatible with the interconversion experiments. Loss of tetra-fluoroethylene from a perfluorocyclobutyl group has precedent elsewhere,¹⁴ and formation of (21) also incorporates a 1,3-fluorine shift. Formation of (22) then follows, from (21), by a simple ring-opening reaction and (23) follows from a further 1,3-fluorine shift.

EXPERIMENTAL

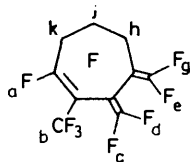
¹⁹F N.m.r. spectra were measured at 40 °C, using a Varian A56/60D or a Bruker HX90E spectrometer, with trichlorofluoromethane as external reference; upfield shifts are quoted as positive. Gas chromatography was carried out using columns packed with 30% silicone gum rubber SE-30 on Chromosorb P (Column O) and 20% di-isodecyl phthalate on Chromosorb P (Column A). Percentage yields quoted were measured either by weighing products or by g.l.c. analysis using a gas density balance detector. I.r. spectra were recorded on a Perkin-Elmer 457 instrument and u.v. spectra on a Unicam SP 8000.

Isomerisation of the Trimer (2).—A mixture of (2) (4.1 g, 8.4 mmol), CsF (2.2 g, 14.5 mmol), and DMF (15 ml) was stirred at room temperature for 24 h. Volatile material was then transferred out under vacuum to a cold trap. The lower fluorocarbon layer was removed, washed with water, dried (P₂O₅), and transferred under vacuum to a cold trap. The resultant liquid (3.4 g) was shown by g.l.c. (columns O and A) to be a single component, subsequently identified as *perfluorospiro[bicyclo[5.2.0]non-1(7)-ene-2,1'-cyclobutane]* (3) (83%), b.p. 147 °C, M⁺ 486 (Found: C, 29.4; F, 70.2. C₁₂F₁₈ requires C, 29.65; F, 70.35%);

ν_{\max} 1 678 cm⁻¹ (C=C); δ_{F} 113.2, 121.0 (AB, J 231 Hz, 4F), 129.8, 133.4 (AB, J 223 Hz, 2F), and unassigned signals between 110.0 and 132.0 p.p.m. (corresponding to 12F).

Pyrolysis of the Product (3).—Dry nitrogen was bubbled through compound (3) (6.64 g, 13.7 mmol) heated to 80 °C, and the reactant was then passed in the stream of nitrogen through a silica tube (30 cm), lined with platinum foil and filled with platinum turnings, at 580 °C. The product was collected in two traps in series, each cooled in liquid air. The nitrogen flow rate gave a contact time of about 30 s. The product (3.94 g) thus obtained was shown by g.l.c.

(columns O and A) to be a complex mixture with four major components, three identified as (21), (22), and (23), and a fourth which was not obtained pure but was identified by comparison with the principal product of a reaction involving pyrolysis over silica;¹⁵ isolated yields were 1.57 g (30%) of (21), 0.41 g (8%) of (22), and 0.29 g (5%) of (23) (by preparative g.l.c. on columns O and A). *Perfluoro-2-methylbicyclo[5.2.0]nona-1(7),2-diene* (21) had b.p. 126 °C (Found:



(22)

C, 31.1; F, 69.3%; M^+ , 386. $C_{10}F_{14}$ requires C, 31.1; F, 68.9%; M , 386; λ_{\max} (cyclohexane) 245 nm ($\log \epsilon$ 4.13); ν_{\max} 1665 cm^{-1} ($-\text{CF}=\text{C}<$); δ_{F} 62.1 [d (J 25) of t (J 10 Hz), 3F], 91.2 (m, 1F), 113.7 (m, 2F), 114.9 (m, 2F), 122.0 (br, s, 4F), and 133.2 (distorted quintet, 2F). *Perfluoro-3,4-dimethylene-2-methylcycloheptene* (22) (Found: C, 31.0; F, 68.4%; M^+ , 386. $C_{10}F_{14}$ requires C, 31.1; F, 68.9%; M , 386) showed λ_{\max} (cyclohexane) 228 nm ($\log \epsilon$ 3.60); ν_{\max} 1740 ($\text{CF}_2=\text{C}<$) and 1690 cm^{-1} ($>\text{C}=\text{CF}-$); δ_{F} 63.6 [d (J 20) of d ($J_{\text{b,c}}$ 11 Hz, 3F_e), 69.6 (q, $J_{\text{b,c}}$ 11 Hz), F_c), 69.8 (d, $J_{\text{d,e}}$ 8 Hz, F_d), 72.6 (t, $J_{\text{g,h}}$ 41 Hz, F_g), 73.2 (d, $J_{\text{d,e}}$ 8 Hz, F_e), 105.4 (m, $J_{\text{d,e}}$ 8 Hz, F_a), 113.4 (d, $J_{\text{g,h}}$ 41 Hz, 2F_h), 118.7 (br, s, 2F_k), and 133.7 (br, s, 2F_j). *Perfluoro-3-methylene-2,4-dimethylcyclohepta-1,4-diene* (23) (Found: C, 30.9%; M^+ , 386. $C_{10}F_{14}$ requires C, 31.09%; M , 386) showed λ_{\max} (cyclohexane) 241 ($\log \epsilon$ 3.68) and 355 nm (ca. 3.48); ν_{\max} 1737 ($\text{CF}_2=\text{C}<$), and 1680 cm^{-1} ($>\text{C}=\text{CF}-$); δ_{F} 64.5 [d (J 20) of d (J 12 Hz), 6F], 67.6 (br, m, 2F), 110.0 (br, m, 2F), and 124.6 (d, J 52, of m, 4F).

In a repeat reaction using a more efficiently lined platinum tube 3.75 g of (3) gave 2.25 g of product. G.l.c. analysis showed that compounds (21), (22) and (23) were present in a 70 : 15 : 15 ratio, but there was no trace of the fourth component.

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REFERENCES

- Part 24, R. D. Chambers, C. G. P. Jones, and G. Taylor, *J. Fluorine Chem.*, in the press.
- Preliminary communication, R. D. Chambers, G. Taylor, and R. L. Powell, *J. Chem. Soc., Chem. Commun.*, 1979, 1062.
- See R. D. Chambers, 'Fluorine in Organic Chemistry,' Wiley-Interscience, New York, 1973, for references to work by a number of authors.
- R. D. Chambers, P. L. Russell, and P. D. Philpot, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1605.
- R. D. Chambers, R. S. Matthews, G. Taylor, and R. L. Powell, *J. Chem. Soc., Perkin Trans. 1*, 1980, 435.
- R. D. Chambers, G. Taylor, and R. L. Powell, *J. Chem. Soc., Perkin Trans. 1*, 1980, 426.
- D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965, p. 221.
- R. D. Chambers, A. A. Lindley, P. D. Philpot, H. C. Fielding, J. Hutchinson, and G. Whittaker, *J. Chem. Soc., Perkin Trans. 1*, 1979, 214.
- Abstracts of Papers, 2nd Chem. Congress N. Am. Continent, Am. Chem. Soc., Las Vegas, August 1980, FLUO 9.
- R. D. Chambers, *J. Fluorine Chem.*, submitted for publication.
- Ref. 3, p. 347.
- J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 1976, 734.
- R. D. Chambers, A. A. Lindley, P. D. Philpot, H. C. Fielding, and J. Hutchinson, *Isr. J. Chem.*, 1978, 17, 150.
- W. J. Feast, R. R. Hughes, and W. K. R. Musgrave, *J. Fluorine Chem.*, 1977, 10, 585.
- R. D. Chambers, J. R. Kirk, and R. L. Powell, in preparation.