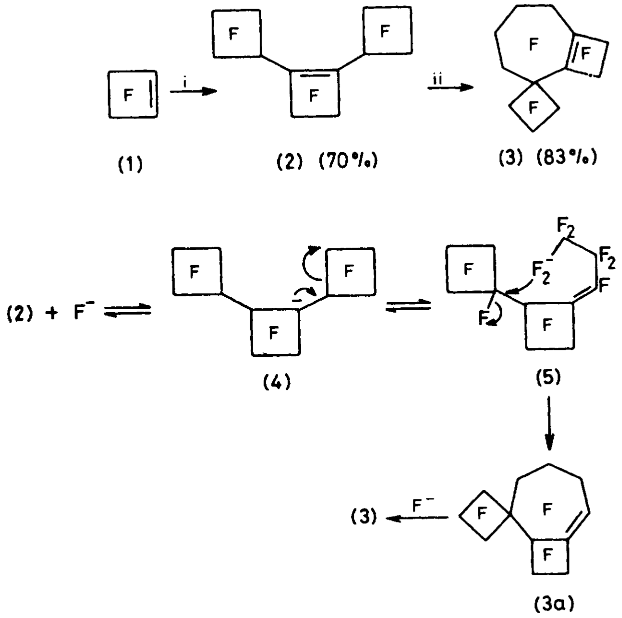
Fluoride Ion-induced Skeletal Rearrangement

By Richard D. Chambers* and Graham Taylor
(*University Science Laboratories, South Road, Durham* DH1 3LE)
and Richard L. Powell
(*I.C.I. Ltd., Mond Division, P. O. Box No. 8, The Heath, Runcorn, Cheshire* WA7 4QD)

Summary Reaction of perfluorocyclobutene trimer (**2**) with caesium fluoride at room temperature gave a surprising rearrangement to the seven-membered ring system (**3**).

We have been pursuing[1] studies into the analogy between the role of fluoride ion, in reactions with unsaturated fluorine containing compounds, and the proton in its reactions with unsaturated hydrocarbons. The analogy includes[2] 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-complexes[3] and carbanions.[4] As we are comparing, in effect, carbocation chemistry with fluorinated carbanion chemistry we would not expect the analogy to include skeletal rearrangements of saturated fluorinated carbanions. Nevertheless, we report here a remarkable rearrangement that involves a saturated fluorinated carbanion.

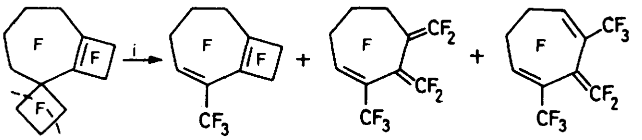
A trimer (**2**) may be obtained by reaction of perfluorocyclobutene (**1**) with pyridine at room temperature.[5] We now find that (**2**) undergoes surprisingly rapid rearrangement in the presence of caesium fluoride in dimethyl formamide (DMF), at room temperature, giving a high yield of a single product (**3**). The structure of (**3**) follows from a combination of spectral data and further reactions, which are outlined later.



Scheme 1. *Reagents*: i, Pyridine; ii, CsF, DMF, room temperature. (The presence of an F-atom 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 and the stage (**4**) → (**5**) is an example of ring-opening of cyclobutylcarbinyl anions, which has ample precedent elsewhere.[6] Anion (**5**) must have a short lifetime in which the integrity of the relatively unstable -CF_2^- is preserved prior to ring-closure. Therefore, we prefer the process (**5**) → (**3a**) over alternatives that could be written but which involve double-bond migration in (**5**), prior to cyclisation. In principle, the ion (**5**) could also form either a 5- or 6-membered ring by attack at other sites in the molecule. Conformational preferences must therefore be responsible for the exclusive formation of (**3**), probably *via* (**3a**).

Proof of the structure of (**3**) comes from a variety of data. The ^{19}F n.m.r. spectrum shows only signals corresponding to CF_2 groups, including two AB-quartets that are typical of a cyclobutane ring. The i.r. spectrum shows a weak absorption at 1678 cm^{-1} (C=C stretch) typical of $(R_F)_2\text{-}C{=}C(R_F)_2$ (R_F = perfluoroalkyl).[7] Remaining proof follows from pyrolysis experiments as illustrated in Scheme 2.



(3) (6) (30%) (7) (8%) (8) (5%)

$(6)\ \text{or}\ (7) \xrightarrow{i} (6) + (7) + (8)$

SCHEME 2. *Reagents*: i, 590 °C, Pt tube, flow system in N_2. (The presence of an F-atom within a ring signifies that all unmarked positions in that ring are attached to fluorine.)

Compound (**3**) was carried in a stream of dry nitrogen through a Pt-lined tube at 590 °C and the product contained compounds (**6**)—(**8**), together with a minor component that has not been characterised. Samples of each compound (**6**)—(**8**) were separated by preparative-scale g.l.c. and were shown by elemental analysis and mass-spectrometry to be isomers of $C_{10}F_{14}$. Furthermore, on recirculation of separate samples of (**6**) and (**7**) through the pyrolysis tube, each gave comparable product mixtures containing (**6**)—(**8**).

The important features indicated by the spectral data for compounds (**6**)—(**8**) are as follows: compound (**6**), $5\times\text{-CF}_2\text{-}$, $CF_3C{=}CF\text{-}$, conjugated system λ = 245 nm (log ϵ 4·13); compound (**7**), $2\times C{=}CF_2$, $CF_3C{=}CF\text{-}$, $3\times\text{-CF}_2\text{-}$, conjugated system λ = 228 nm (log ϵ 3·57). Compound (**8**) illustrates these points, having $2\times\text{-CF}_2\text{-}$, δ_F 124 p.p.m. (from $CFCl_3$), $2\times CF_3C{=}C$ 64 p.p.m. (d of d, J 20 and 12 Hz), $2\times C{=}CF$ 110 p.p.m. (br), $C{=}CF_2$ 67 p.p.m. (br), conjugated system λ = 241 nm (log ϵ 3·68). Two structures are possible for the latter compound but only (**8**) is compatible with the conversion (**6**) or (**7**) → (**6**)—(**8**). The full data are then easily rationalised in the structures shown in Scheme 2 and this accounts for the interconversion of (**6**) and (**7**) through the well-known cyclobutene–butadiene equilibrium. Furthermore, the relationship of compounds (**6**) and (**7**) with compounds (**3**) and (**8**) is explained by these structures.

These experiments provide an easy route to a variety of new seven-membered ring systems, essentially starting with perfluorocyclobutene (**1**), and the further chemistry of these compounds is being investigated.

(*Received*, 23*rd July* 1979; *Com.* 789.)

---

[1] See R. D. Chambers, A. A. Lindley, P. D. Philpot, H. C. Fielding, J. Hutchinson, and G. Whittaker, *J.C.S. Perkin I*, 1979, 214, and earlier parts of the series.

[2] See R. D. Chambers, 'Fluorine in Organic Chemistry,' Wiley-Interscience, New York, 1973, for references to work by a number of authors.

[3] R. D. Chambers, P. L. Russell, and P. D. Philpot, *J.C.S. Perkin I*, 1977, 1605.

[4] R. D. Chambers, R. S. Matthews, G. Taylor, and R. L. Powell, *J.C.S. Perkin I*, in the press.

[5] R. D. Chambers, G. Taylor, and R. L. Powell, *J.C.S. Chem. Comm.*, 1978, 433.

[6] D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965, p. 221.

[7] R. D. Chambers, A. A. Lindley, P. D. Philpot, H. C. Fielding, and J. Hutchinson, *Israel J. Chem.*, 1978, **17**, 150.