# Photochemically-induced 1,3-Fluorine Shifts. The Synthesis of Novel Fluorinated Spiro Compounds

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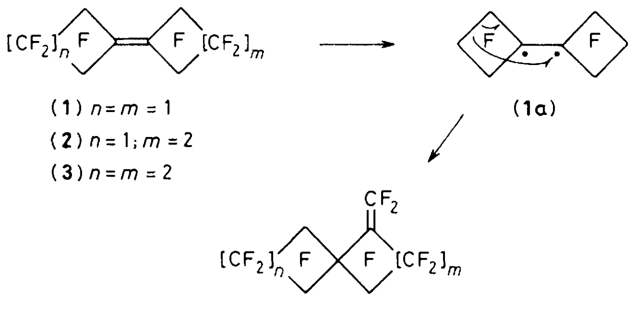
The perfluorocyclobutene derivative (**8**) undergoes a photochemically-induced 1,3-fluorine shift followed by skeletal rearrangement; the preparation of novel spiro compounds is described.

In earlier work we have emphasised the value of fluorine and perfluoroalkyl groups as 'passive' substituents for the investigation of photochemically- and thermally-induced skeletal rearrangements.[1] Sigmatropic migrations of fluorine atoms have been described by various workers[2] but in many cases there is an ambiguity that is difficult to resolve between the possibility of concerted 1,3-shifts of fluorine and rearrangements induced by adventitious fluoride ion. Here, we describe a clear-cut example of a photo-equilibrium involving fluorine migration, followed by skeletal rearrangements to produce novel spiro derivatives.[3]

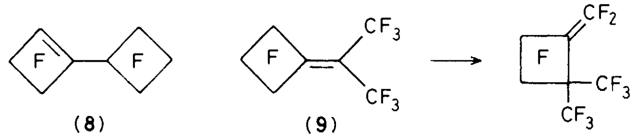
Irradiation of alkene (**1**), or a 1 : 1 mixture of alkenes (**1**) and (**8**), at 254 nm for 7 days in the presence of a trace of mercury, produced spiro compound (**4**) in 95% yield.† The most likely route to (**4**) involves a 1,3-perfluoroalkyl shift in the diradical (**1a**), formed from the olefin (**1**). Furthermore, it is clear that, in the present case, the photoequilibrium (**8**)$\rightleftharpoons$(**1**) involves a genuine 1,3-allylic shift of fluorine and is not induced by traces of fluoride ion present in the system, because, in a separate experiment with added caesium fluoride photolysis of (**1**), or of a mixture of (**1**) and (**8**), yielded dimer (**11**) in 85% yield. Similarly, irradiation of alkenes (**2**) and (**9**) produced compounds (**5**) and (**10**), respectively, in essentially quantitative yields and in the presence of fluoride ion, photolysis of (**2**) gave dimer (**12**). Compound (**5**) was assigned the structure shown, rather than the isomeric structure (**6**), on the basis of i.r. data.‡ However, under these conditions, perfluorobicyclopentylidene (**3**) was recovered unchanged in contrast to the earlier observation of a rearrangement to spiro-alkane (**7**).[2d] This contrast between (**1**) and (**3**) demonstrates increased reactivity due to ring strain in the four membered ring systems compared with the bicyclopentylidene system.



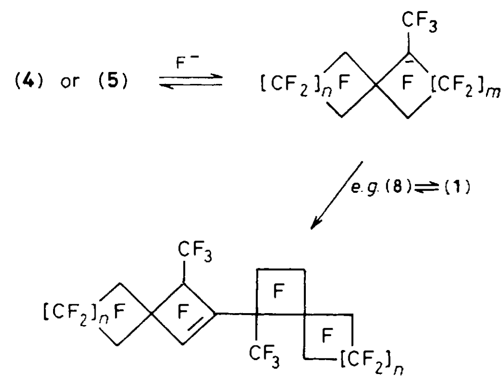
(**1**) $n = m = 1$
(**2**) $n = 1; m = 2$
(**3**) $n = m = 2$

(**1a**)

(**4**) $n = m = 1$
(**5**) $n = 2; m = 1$
(**6**) $n = 1; m = 2$
(**7**) $n = m = 2$



(**8**) (**9**) (**10**)



(**11**) $n = 1$
(**12**) $n = 2$

All compounds are perfluorinated. F in the centre of a ring indicates all unmarked bonds to fluorine.

The formation of (**11**) and (**12**), from (**4**) and (**5**) respectively, involves a simple fluoride-ion induced dimerisation. Compounds (**11**) and (**12**) show satisfactory mass-spectral and n.m.r. data, *e.g.* the appropriate intensity corresponding to CF$_3$ and CF$_2$ resonances are observed in the $^{19}$F n.m.r. spectra. More revealing, however, are the absorptions at $\delta_F$ 97.3 and 96.1 p.p.m. (each intensity 1) which correspond to vinylic fluorine atoms, and at 184.4 and 177.0 p.p.m. (each intensity 1) which are distinctive for 'tertiary fluorine', for (**11**) and (**12**), respectively. These data clearly reveal structures (**11**) and (**12**) rather than isomers without vinylic fluorine sites, which normally would be anticipated.

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## References

1 See, for example, R. N. Barnes, R. D. Chambers, R. D. Hercliffe, and R. Middleton, *J. Chem. Soc., Perkin Trans. 1*, 1981, 3289, and references cited therein.

2 (a) G. Camaggi and F. Gozzo, *J. Chem. Soc. C*, 1971, 925; (b) W. J. Feast and W. E. Preston, *J. Chem. Soc., Chem. Commun.*, 1974, 985; (c) A. N. Bell, R. Fields, R. N. Haszeldine, and I. Kumadaki, *ibid.*, 1975, 866; (d) J. V. Drayton, W. T. Flowers, R. N. Haszeldine, and T. A. Parry, *ibid.*, 1976, 490.

3 For analogous thermal rearrangements of some closely related hydrocarbon systems see P. LePerchec and J. M. Conia, *Tetrahedron Lett.*, 1970, 1587; W. J. Dolbier, K. Akiba, J. M. Riemann, C. A. Harmon, M. Bertrand, A. Bezaguet, and M. Santelli, *J. Am. Chem. Soc.*, 1971, **93**, 3933; L. K. Bee, J. W. Everett, and P. J. Garrett, *Tetrahedron*, 1977, **33**, 2143.

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† Satisfactory elemental analyses were obtained for all new compounds recorded here.

‡ The C=C absorption for both (**4**) and (**5**) occurs at the same frequency. It is well known that the absorption frequency of exocyclic C=C bonds decreases with increasing ring size.