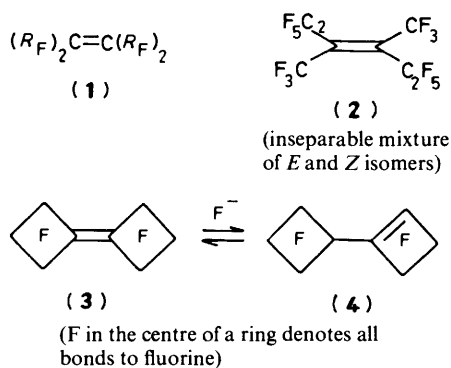# Reactions Involving Fluoride Ion. Part 31.† Remarkable Reactivity of Perfluoro-bicyclobutylidene

Andrew E. Bayliff, Martin R. Bryce, Richard D. Chambers,* Julian R. Kirk, and Graham Taylor
Department of Chemistry, University of Durham, South Road, Durham, DH1 3LE

Perfluorobicyclobutylidene (3) readily forms cycloadducts with butadiene, cyclopentadiene, 6,6-dimethylfulvene and furan, whereas perfluoro-3,4-dimethylhex-2-ene (2) is unreactive under the same conditions. This marked difference in reactivity between (2) and (3) is attributed to angle strain in (3). Reaction of the alkene (3) with cyclohexa-1,3-diene yields 1H,1'H-perfluorobicyclobutyl (9) and benzene, by hydrogen transfer. The alkene (3) undergoes an 'ene' reaction with propene. Epoxides of perfluorobicyclobutylidene (3) and perfluorobicyclopentylidene (11) have been prepared; they both show high thermal stability and the latter epoxide fragments in the presence of fluoride ion to yield perfluorocyclopentene and perfluorocyclopentanone.

There are many examples of small carbocyclic systems where high reactivity is attributed to ring strain [1] but it is often difficult to have appropriate models which assist in the separation of electronic effects and effects of ring strain. Highly fluorinated alkenes present unusual aspects of reactivity in cycloaddition reactions and we are continuing to explore the chemistry of perfluoro(polyalkylethenes) (1) in cycloaddition processes.[2]

In the course of work leading to more sophisticated compounds from simple, unsaturated fluorocarbons we have obtained the interesting fluorinated alkenes (2)—(4).[3] Compounds (2) and (3) form an especially fascinating pair for the

$(R_F)_2C=C(R_F)_2$

(1)

(2)

(inseparable mixture of E and Z isomers)

(3)   (4)

(F in the centre of a ring denotes all bonds to fluorine)

purpose of illustrating the effect of strain on reactivity since, formally, both systems have four perfluoroalkyl groups attached to a double bond and hence very similar electronic environments. Compound (3) has, however, considerable angle strain and the success of the various addition reactions described here for (3) in comparison with (2) derives from this.[4] Isomers (3) and (4) are of comparable stability because they are obtained in approximately equal proportions from systems equilibrated by fluoride ion.[5]

We have already discussed the fact that addition of diazomethane to systems of type (1) occurs remarkably readily, whereas successive replacement of perfluoroalkyl by fluorine at the double bond leads to progressively reduced reactivity.[2] We have attributed these observations to lowering of the LUMO energy of the alkene by perfluoroalkyl substituents. In consequence we expected reasonable reactivity of systems of the type (1) towards dienes, but we have now found that (2) is

unreactive to a range of dienes, even under forcing conditions. This is in striking contrast to perfluorobicyclobutylidene (3) which reacts with butadiene at 80 °C in a Carius tube to give a high yield of the Diels–Alder adduct (5).

$(3) + (CH_2{=}CH)_2 \longrightarrow$

(5)
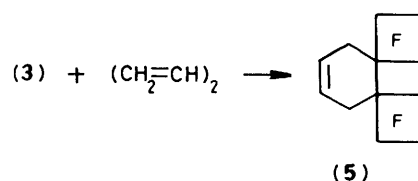
Cyclopentadiene, 6,6-dimethylfulvene, and furan similarly reacted with (3) to afford adducts (6), (7), and (8), respectively, whose structures followed simply from spectroscopic data.


(6) X = CH$_2$

(7) X =

(8) X = O
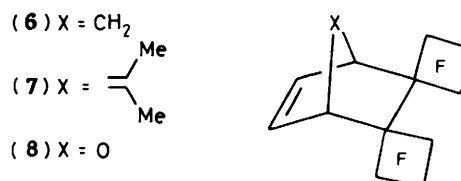
Cyclohexa-1,3-diene also reacted with (3) under the same conditions but, in this case, we did not observe any cycloadduct; instead, the products were the alkane (9) (90%) and benzene

(3)

(9)
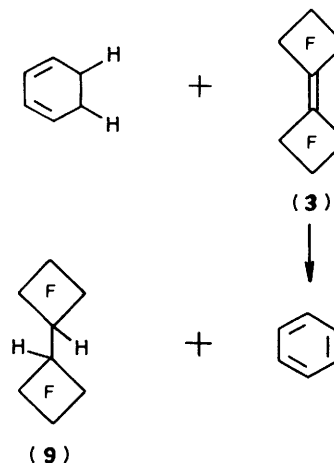
(83%), *i.e.* transfer of hydrogen, rather than cycloaddition, had occurred. Such processes have been observed in other reactions involving cyclohexa-1,3-diene;[6] in particular $(CF_3)_2C=C(CN)_2$ reacts in this way,[7] although the isomeric compound $CF_3(CN)C=C(CN)CF_3$ yields a $[4\pi + 2\pi]$ cycloadduct.[8] It seems reasonable to consider the formation of (9) from (3) and cyclohexa-1,3-diene to be a concerted process, and this would correspond with the fact that, as we have also shown, reaction of compound (3) with propene gives the 'ene' product (10). It would seem a short extrapolation from an 'ene' reaction to a concerted $[4\sigma + 2\pi]$ process in the reaction with cyclohexa-1,3-diene.

(10)
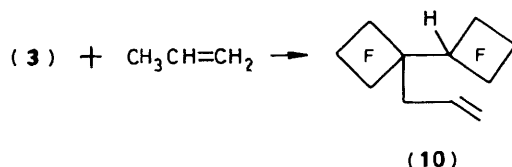
Although systems of type (1) are potentially reactive in cycloaddition reactions by virtue of their low LUMO energies, the lack of reactivity observed so far for (2) can be attributed to steric hindrance to the approach of dienes, arising from the perfluoroalkyl groups. In referring to the steric effects of perfluoroalkyl, it is worthwhile emphasising that, with so many non-bonding electron pairs on fluorine atoms, a perfluoroalkyl group will have steric effects considerably in excess of the corresponding alkyl group. We have also had little success in additions of 1,3-dipoles to (2), other than with diazomethane,[9] and again we attribute this to steric effects. The considerable reactivity of (3) towards dienes could therefore result from a combination of angle strain and reduced steric effects arising from incorporation of the perfluoroalkyl groups into a ring. We have been able to investigate the latter effect by considering perfluorobicyclopentylidene (11). Under the same conditions (11) was also unreactive to cyclopentadiene and furan. Since the geometries of (3) and (11) are so similar we can attribute the major difference in reactivity between (3) and (11) to the effect of angle strain in (3).

(11)   (12)

Isomer (4) was also unreactive towards dienes and the reasons for this are less immediately obvious since we have argued that (3) and (4) are of comparable stability. Nevertheless, in an earlier paper,[5] we explained that the reason for observing comparable amounts of (3) and (4) under equilibrium conditions is that angle strain is much greater in (3) than in (4), otherwise only the *exo* isomer (3) would be observed as is the case in the five-membered system (11). This marked difference in reactivity between isomers (3) and (4) has enabled reactions of (3) with dienes to be carried out using a mixture of (3) and (4) in the presence of caesium fluoride. Under these conditions no (4) is recovered and yields of adducts are the same as when pure (3) is used. Also compound (3), during its formation from perfluorocyclobutene in the presence of pyridine has been trapped by cyclopentadiene to yield (6).

We can conclude from all these arguments that the angle strain in (3) arising from an unsaturated site in *both* rings, offsets any steric problems of cycloaddition. Supporting this con-

clusion, compound (12), with an unsaturated site in only one ring, was also unreactive towards dienes under the present conditions.

The outstanding reactivity of (3) was also reflected in the addition of bromine, albeit slowly, to yield (13), whereas, again, the alkene (2) was unreactive. More surprisingly, a co-polymer was formed from a 1:1 mixture of (3) and butadiene activated by γ-rays, whereas (2) is not incorporated in a similar process; indeed polymerisation of butadiene is inhibited by the presence of (2). We have recently reported the formation and fluoride ion-induced ring opening of a range of perfluoroalkyl substituted epoxides[10] and we have now prepared the spiro epoxides (16) and (17) from the parent alkenes. Compounds (14) and (15)

(13) X = Br
(14) X = Cl

(15)
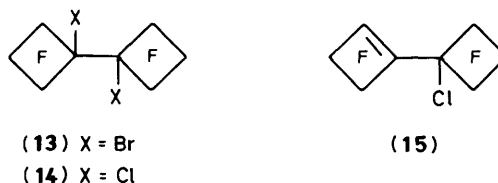
were formed alongside the epoxide (16). The latter is remarkably stable and is recovered unchanged after being heated at 300 °C for 2 h. This stability has been observed previously for other fluorocarbon epoxides,[10] but contrasts with the hydrocarbon analogue (19) which isomerises quantitatively to the spirocyclopentanone (20) at 200 °C.[11] Attempted ring opening of the epoxide (16), by reaction with caesium fluoride, gave a complex mixture of unidentified products. However, the epoxide (17), when heated in the presence of fluoride ion yielded perfluorocyclopentene and perfluorocyclopentanone, presumably *via* the process shown in the Scheme, *via* (18).

(16)   (19)   (20)

(17)   (18)
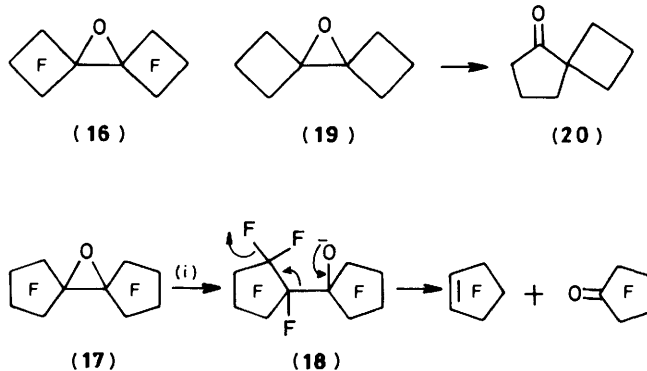
(i) CsF, 200 °C, 16 h.

Scheme.

Experimental

Details of instrumentation have been discussed previously.[12] γ-Irradiation was produced using a ^{60}Co source (*ca.* 500 Curies).

Reactions of Perfluorobicyclobutylidene (3).—(a) *With butadiene.* A mixture of the alkene (3) (1.25 g, 3.9 mmol) and butadiene (0.85 g, 15 mmol) was heated in a sealed Carius tube at 80 °C for 36 h. Volatile material was transferred under vacuum to yield the *adduct* (5) (1.04 g, 72%) as a colourless liquid (Found: C, 38.1; H, 1.8; F, 60.0. $C_{12}H_6F_{12}$ requires C, 38.1; H, 1.6; F, 60.3%); *m/z* 378 (M^+); δ_F (CFCl$_3$) 114—130; δ_H (CFCl$_3$) 5.8 (2 H, s) and 1.4 (4 H, s).

(b) *With cyclopentadiene.* A mixture of the olefin (3) (1.25 g, 3.9 mmol) and cyclopentadiene (0.35 g, 4.6 mmol) was heated in a sealed Carius tube at 80 °C for 16 h. The resultant liquid was purified by preparative scale g.l.c. to yield the *adduct* (6) (1.50 g, 70%) as a colourless liquid (Found: C, 40.0; H, 1.5; F, 58.5. $C_{13}H_6F_{12}$ requires C, 40.3; H, 1.7; F, 58.2%); m/z 390 (M^+); δ_F (CFCl$_3$) 112—124.3 (8F) and 130.3 and 134.7 (AB, 4F, J 229 Hz); δ_F (CFCl$_3$) 6.00 (2 H, s), 3.13 (2 H, s), and 1.13 (2 H, s). The same adduct (6) was isolated in 76% yield when a 1:1 mixture of dienes (3) and (4) (1.25 g, 3.9 mmol), caesium fluoride (0.6 g, 3.7 mmol), and cyclopentadiene (0.35 g, 4.6 mmol) were allowed to react under conditions identical with those described above.

(c) *With 6,6-dimethylfulvene.* A 1:1 mixture of alkenes (3) and (4), caesium fluoride (0.25 g, 1.6 mmol), and 6,6-dimethylfulvene (0.46 g, 4.3 mmol) was heated in a sealed Carius tube for 5 h at 80 °C. Vacuum transfer separated a colourless oil which solidified with time. Vacuum sublimation (100 °C, 0.1 mm Hg) afforded the *adduct* (7) (0.58 g, 57%) as colourless crystals, m.p. 71—73 °C (Found: C 44.7; H, 2.3; F, 52.7. $C_{16}H_{10}F_{12}$ requires C, 44.7; H, 2.3; F, 53.0%); m/z 430 (M^+); δ_F (CFCl$_3$) 114—135; δ_H (CFCl$_3$–CDCl$_3$) 6.56 (2 H, br, s), 4.06 (2 H, br, s), and 1.64 (6 H, s).

(d) *With furan.* A 1:1 mixture of dienes (3) and (4) (0.76 g, 2.3 mmol), caesium fluoride (0.25 g, 1.6 mmol) and furan (0.34 g, 5.0 mmol) was heated in a sealed Carius tube at 100 °C for 20 h. Vacuum transfer separated the *adduct* (8) (0.46 g, 50%) as a colourless liquid (Found: C, 37.0; H, 0.8; F, 58.5. $C_{12}H_4F_{12}O$ requires C, 36.7; H, 1.0; F, 58.2%); m/z 392 (M^+); δ_F (CFCl$_3$) 113—134; δ_H (CDCl$_3$–CFCl$_3$) 6.4 (2 H, s) and 4.5 (2 H, s).

(e) *With cyclohexa*-1,3-*diene.* A mixture of the alkene (3) 0.55 g, 1.70 mmol) and cyclohexa-1,3-diene (0.27 g, 2.8 mmol) was heated in a sealed Carius tube at 80 °C for 24 h. Volatile material was purified by preparative scale g.l.c. to yield 1H,1'H-*perfluorobicyclobutyl* (9) as a colourless liquid (0.50 g, 90%) (Found: C, 29.8; H, 0.7; F, 70.0. $C_8H_2F_{12}$ requires C, 29.4; H, 0.6; F, 70.0%); m/z 326 (M^+); δ_F (CFCl$_3$) 113.7 and 129.0 (4 F, AB, J 226 Hz), 130.3 and 135.3 (2 F, AB, J 226 Hz); δ_H (CFCl$_3$) 3.33 (br, s); and benzene (0.11 g, 83%).

(f) *With propene.* A mixture of the alkene (3) (0.55 g, 1.70 mmol) and propene (0.42 g, 10 mmol) was heated at 100 °C for 18 h in a sealed Carius tube. Volatile material was vacuum transferred to yield the *adduct* (10) (0.24 g, 40%) as a colourless liquid (Found: C, 35.8; H, 1.8; F, 62.3. $C_{11}H_6F_{12}$ requires C, 36.1; H, 1.6; F, 62.3%); m/z 366 (M^+); δ_F (CFCl$_3$–CDCl$_3$) 110—132; δ_H (CFCl$_3$–CDCl$_3$) 5.5 (3 H, m), 3.4 (1 H, s), and 3.0 (2 H, d, J 5.5 Hz).

(g) *With bromine.* A mixture of the alkene (3) (2.13 g, 6.6 mmol) and bromine (1.05 g, 6.6 mmol) was left at room temperature for 24 h and then heated at 60 °C for a further 4 h to give a colourless liquid which on distillation yielded 1,1'-*dibromotetradecafluorobicyclobutyl* (13) (2.5 g, 80%), b.p. 165 °C (Found: C, 19.7; Br, 33.5; F, 46.6. $C_8Br_2F_{12}$ requires C, 19.8; Br, 33.1; F, 47.1%); m/z 405 ($M^+ - {}^{81}Br$); δ_F (CFCl$_3$) 103.4 and 120.3 (2 F, AX, J 208 Hz), and 123.7 and 127.8 (2 F, AB, J 225 Hz).

(h) *With butadiene under γ-Irradiation.* A mixture of the alkene (3) (1.6 g, 5.0 mmol) and butadiene (0.31 g, 6.0 mmol) was irradiated with γ-rays for 12 h. The resulting oily solid was identified as a copolymer of the alkene (3) and butadiene, of approximate stoicheiometry 1:1 [Found: C, 43.1; H, 1.9; F, 54.3. $(C_{12}H_6F_{12})_n$ requires C, 38.1; H, 1.6; F, 60.3%].

Epoxidation of Perfluorobicyclobutylidene (3).—A mixture of the alkene (3) (5.0 g, 15.2 mmol), calcium hypochlorite * (4.4 g, 30.7 mmol), and acetonitrile (15 ml) was stirred at room temperature for 48 h. Volatile material was transferred *in vacuo* to a cold trap and the resulting lower layer purified by preparative scale g.l.c. to yield *perfluoro-9-oxadispiro-* [3.0.3.]*nonane* (16) (3.1 g, 57%) (Found: C, 27.9; F, 66.7. $C_8F_{12}O$ requires C, 28.3; F, 67.0%), m/z 271 ($M^+ - CF_3$); δ_F (CFCl$_3$) 123.2 and 132.3 (8 F, AB, J 244 Hz), 135.4 and 138.3 (4 F, AB, J 225 Hz); v_{max} 1 382, 1 320, 1 300, 1 220, 1 140, 1 016, 938, 890, 760, 620, and 560 cm^{-1}; 1,1'-*dichlorotetra-decafluorobicyclobutyl* (14) (0.6 g, 10%) (Found: C, 24.5; F, 57.0; Cl, 18.6. $C_8F_{12}Cl_2$ requires C, 24.3; F, 57.7; Cl, 18.0%); m/z 294 ($M^+ - C_2F_4$); δ_F (CFCl$_3$) 114.3 and 122.1 (8 F, br AB, J 205 Hz), and 127.4 and 129.1 (4 F, AB, J 225 Hz); v_{max} 1 382, 1 220, and 1 000 cm^{-1}; 1-(1'-*chloroheptaflurocyclobutyl)cyclobut-1-ene* (15) (0.5 g, 10%) (Found: C, 28.2; F, 57.6; Cl, 12.1. C_8ClF_{11} requires C, 28.2; Cl, 10.4; F, 61.4%); m/z 340 (M^+); δ_F (CFCl$_3$) 97.3 (1 F, br, s), 116.3 (2 F, m), 121.3 (2 F, m), 122.4 (4 F, s), and 128.9 (2 F, s); v_{max} 1 715, 1 220, and 1 160 cm.$^{-1}$

Epoxidation of Perfluorobicyclopentylidene (11).—A mixture of the alkene (11) (8.4 g, 19.1 mmol), calcium hypochlorite (5.7 g, 40 mmol), and acetonitrile (31 ml) was stirred at room temperature for 72 h. Work-up as for compound (16) afforded *perfluoro-11-oxadispiro[4.0.4.1]undecane* (17) (3.3 g, 38%) (Found: C, 27.6; F, 69.3. $C_{10}F_{16}O$ requires C, 27.3; F, 69.1%); m/z 440 (M^+); δ_F (CFCl$_3$) 117.8 and 129.0 (8 F, AB, J 273 Hz), 137.8 (8 F, s); v_{max} 1 336, 1 313, 1 282, 1 215, 1 035, 962, 909, 728, 668, 575, and 408 cm.$^{-1}$

Reaction of the Epoxide (17) *with Caesium Fluoride.*—The epoxide (17) (2.0 g, 4.5 mmol) and caesium fluoride (0.62 g, 4.1 mmol) contained in a sealed tube were heated at 200 °C for 16 h. Volatile material (1.6 g) was collected in a cold trap and identified as a mixture of perfluorocyclopentene (83%) and perfluorocyclopentanone (57%) by comparison of i.r. and ^{19}F n.m.r. spectra with authentic samples and literature data.[14]

References

1 For example see K. P. C. Vollhardt, *Pure Appl. Chem.* 1980, **52**, 1645 and references therein; A. Greenberg and J. F. Liebman, 'Strained Organic Molecules,' Academic Press, New York, 1978.

2 M. R. Bryce, R. D. Chambers, and G. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1984, 509.

3 R. D. Chambers, J. R. Kirk, and G. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1982, 673, and earlier parts of a series.

4 For a preliminary communication see R. D. Chambers, J. R. Kirk, G. Taylor, and R. L. Powell, *J. Fluorine Chem.*, 1983, 393.

5 R. D. Chambers, G. Taylor, and R. L. Powell, *J. Chem. Soc., Perkin Trans. 1*, 1980, 429.

6 Y. Kobayashi, M. Honda, Y. Hanzawa, I. Kumadaki, and A. Ohsawa, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1743.

7 W. J. Middleton, *J. Org. Chem.*, 1965, 1402; *J. Fluorine Chem.*, 1981, 397.

8 S. Proskow, H. E. Simmons, and T. L. Cairns, *J. Am. Chem. Soc.*, 1963, **85**, 2341; *ibid*, 1966, **88**, 5254.

9 M. R. Bryce and R. D. Chambers, unpublished results.

10 M. R. Bryce, R. D. Chambers, and J. R. Kirk, *J. Chem. Soc., Perkin Trans. 1*, 1984, 1391.

11 L. K. Bee, J. Beeby, J. W. Everett, and P. J. Garratt, *J. Org. Chem.*, 1975, **40**, 2212.

12 M. R. Bryce, R. D. Chambers, A. A. Lindley, and H. C. Fielding, *J. Chem. Soc., Perkin Trans. 1*, 1983, 2451.

13 P. L. Coe and co-workers, Lecture at the 'Winter Fluorine Symposium,' American Chemical Society, Daytona Beach, 1983.

14 L. G. Anello, A. K. Price, and R. F. Sweeney, *J. Org. Chem.*, 1968, **33**, 2692.

15 R. N. Barnes, R. D. Chambers, C. D. Hewitt, M. J. Silvester, and E. Klauke, *J. Chem Soc., Perkin Trans 1*, 1985, 53.

* Other workers[13] have also described the direct use of solid calcium hypochlorite.