Reactions Involving Fluoride Ion. Part 30.[1] Preparation and Reactions of Epoxides Derived from Perfluoroalkyl Substituted Alkenes

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Reactions of alkenes that are oligomers of tetrafluoroethene or hexafluorocyclobutene with sodium hypochlorite give epoxides which show remarkable overall stability. Ring-opening reactions, induced by fluoride ion, yield alkenes, ketones, and acid fluorides.

There is continued interest in the chemistry of fluorinated epoxides. They have been found to undergo several reactions of synthetic and mechanistic interest and their potential as monomers for the preparation of fluorinated polyethers of industrial importance is well recognised.

Preparation of Fluorinated Epoxides.—Partially fluorinated epoxides have long been accessible by treatment of halohydrins[2] or halogenoacetates[3] with base, or by addition of a carbene to a fluorinated aldehyde or ketone.[4] More recently several routes have been developed to perfluorinated epoxides since the first general synthesis reported in 1962, using alkaline hydrogen peroxide at low temperatures.[5] The latter method was found to be applicable to numerous perfluoroalk-1-enes, perfluoro-cycloalkenes, and certain perfluorinated internal alkenes but tetrafluoroethene oxide could not be prepared by this method. However, the epoxides of both tetrafluoroethene and hexafluoropropene can be prepared by reaction of the olefins either with molecular oxygen under free radical conditions,[6] or with the acid fluoride of permanganic acid ($FMnO_3$).[7] Another unusual method of epoxidation utilises the reaction of certain perfluoroalkenes with oxygen difluoride.[8] Hexafluoroacetone had been converted into perfluoro-2,3-dimethylbutane 2,3-oxide by two methods: coupling with triethyl phosphite, or by addition of bis(trifluoromethyl)carbene.[9] It is noteworthy that of the many epoxide syntheses developed few produce epoxides from internal fluoro-olefins in significant yield. However, Russian workers have developed a procedure using hypochlorite to give good yields of internal epoxides, with retention of stereochemistry,[10] and using this method Coe et al. have epoxidised several fluorocarbon alkenes[11] and a perfluoroalkyl substituted ketene to yield a remarkably stable α-lactone.[12]

We have a continued interest in developing the chemistry of novel fluorinated alkenes and in this paper we describe the preparation and reaction of some new epoxides derived from internal perfluoroalkenes. In particular, we report the first epoxides from perfluorotetra-alkylethenes, whereas most of the earlier work had been concerned with epoxides from mono- or bis-perfluoroalkylated fluoroethenes. The epoxides (1)—(5) have been prepared in good yield by reaction of the parent alkene with aqueous sodium hypochlorite in the presence of acetonitrile. It should be noted that although the hypochlorite solution contains a large excess of hydroxide ions, nucleophilic attack on the fluoroalkene by OH^- is not observed; the enhanced nucleophilicity of OCl^- compared to OH^- can be explained by the presence of a high energy HOMO for the former.[13]

Complete retention of configuration was observed in the formation of the epoxide (1) but to a lesser extent for the epoxide (2) where the parent olefin as a mixture of (E) (80%) and (Z) (20%) stereoisomers yielded the epoxide (2), containing a mixture of (E) (73%) and (Z) (27%) stereoisomers as judged by


(1)
(E:Z isomers 1:1)

(2)

(3)

(4)

(5)

(6)
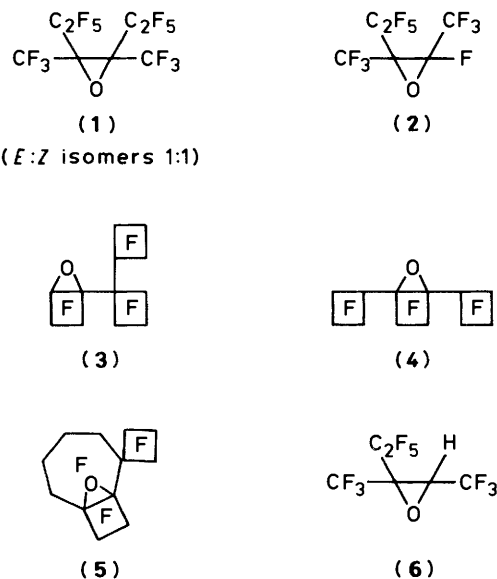
(F in the centre of a ring denotes all unmarked bonds to F)

[19]F n.m.r. spectroscopy. While this work was in progress other workers[11b] have reported on this reaction and they observe lower stereospecificity than our own. It is not clear why bond rotation before ring closure and consequent loss of stereochemistry should occur in this case but not with alkenes with fewer perfluoroalkyl groups on the double bond.[10]

Epoxidation of the alkene (7) gave compound (6) (28%) as an unexpected by-product alongside the epoxide (1); formally a C_2F_5 group of (1) has been replaced by a hydrogen atom but control experiments showed that (1) could not be transformed into (6) under the present conditions. The likely mechanism of formation of both (1) and (6) is shown in Scheme 1. The anion (8) may either ring close to form (1), or eliminate fluoride ion by allylic displacement to form (9), which undergoes hydrolysis eventually giving (10). In the final step, ring closure of (10) occurs exclusively giving the epoxide (6); an alternative elimination of F^- from (10) does not occur as the product would contain a terminal CF_2 group. As would be expected, stereochemistry is not retained during the formation of (6); the observed $Z:E$ isomer ratio in (6) is 2.5:1, indicative of the different steric requirements of the CF_3 and C_2F_5 groups. Evidence for this mechanism of formation of (6) comes from the identification of the $CF_3CO_2^-$ anion in the [19]F n.m.r. spectrum of the aqueous layer of the reaction mixture. There is a precedent for the loss of a C_2F_5 group in reactions of alkene (7) with nucleophiles,[14] although this appears to be the first reported case of such a fragmentation occurring with epoxidation.
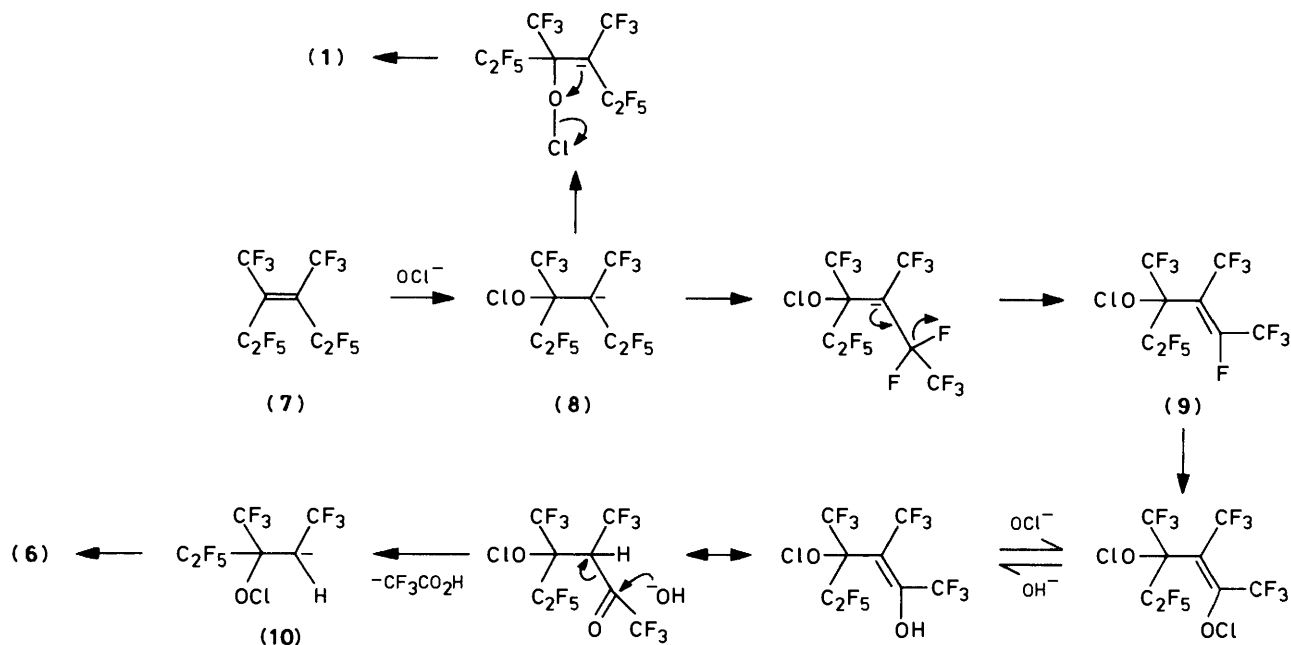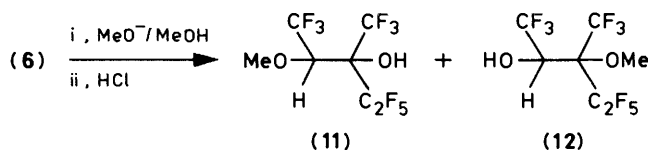
Scheme 1.

Reactions of Fluorinated Epoxides.—Many fluorocarbon epoxides react readily with nucleophiles, typically with ring opening followed by loss of fluoride ion.[2a,15] In an unsymmetrically substituted epoxide initial nucleophilic attack preferentially occurs at the more substituted ring carbon,[16] unless this carbon is very hindered,[17] or the nucleophile is very bulky,[18] when attack is diverted to the less substituted carbon. The final product is thus a ketone or a carbonyl fluoride. Alternatively, it is possible for the anion produced by ring opening to act as a nucleophile for a second epoxide molecule leading to oligomers of industrial importance.[19] In contrast, reactions of fluoro-epoxides with electrophiles require very forcing conditions.[10a] We now describe the chemistry of epoxides (1)—(6), some of which undergo novel fluoride ion-induced reactions.

The striking feature of epoxides (1)—(6) is their overall stability. This is probably due to the bulky, electronegative perfluoroalkyl groups both hindering attack of the nucleophile and withdrawing electrons from the ring. Thus compound (1) was recovered unchanged under the following conditions: (*a*) passage over CsF at 240 °C in a flow of nitrogen; (*b*) passage through a platinum-lined tube at 530 °C in a flow of nitrogen; (*c*) stirring with caesium fluoride in an aprotic solvent at 20 °C for 16 h; (*d*) stirring with methoxide ion, or n-butyl-lithium, at 20 °C for 16 h; (*e*) stirring with acetaldehyde under γ irradiation at 20 °C for 40 h. Pyrolysis of the pure *Z* isomer of the epoxide (1) at 200 °C for 16 h produced a 1:1 mixture of *E* and *Z* isomers of (1), but attempts to trap a possible radical intemediate with either bromine or cyclohexene were unsuccessful. We had anticipated that thermal cleavage might occur to yield ketone and carbene fragments but this was not observed on any occasion.

Compound (6) also shows great thermal stability and is unchanged at 580 °C in a flow pyrolysis reaction and was quantitatively recovered from static pyrolysis at 200 °C in the presence of fluoride ion. No reaction was observed between (6) and acetaldehyde under free radical conditions, and the proton was unaffected by diazomethane or sodium metal. However, (6) is more susceptible to nucleophilic attack than (1), as methoxide ion reacts with (6) at room temperature to give, initially, a stable salt in solution which on acidification yields a mixture of the

alcohols (11) and (12). This is consistent with initial attack of methoxide at both of the ring carbons of epoxide (6).


Efficient ring opening of the epoxides (1)—(5) was achieved, however, by heating at 200 °C with CsF in a sealed tube. Thus, the epoxide (1) was converted into a 1:1 mixture of perfluorobutan-2-one and perfluorobut-2-ene (Scheme 2). The
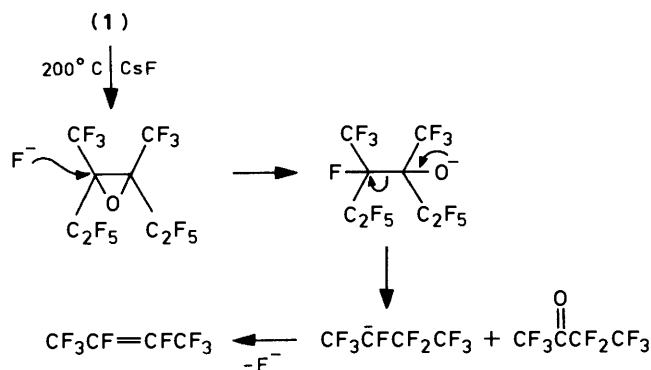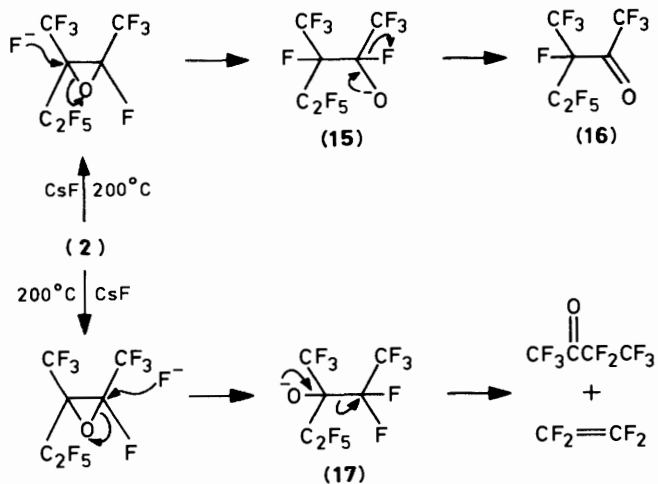

Scheme 2.

latter did not dimerise under the reaction conditions probably because ketones are known to form stable complexes with CsF, thereby removing active fluoride from the system.[20] The epoxide (4), the only other symmetrical epoxide studied, underwent similar cleavage, followed by further reaction of the ketone fragment, to yield perfluorocyclobutene and the acid fluoride (14) (Scheme 3). The presence of an acid fluoride group (14) was apparent from spectral data; a carbonyl absorption at 1 885 cm⁻¹ in the i.r. spectrum, and a single fluorine at −18 p.p.m. in the ¹⁹F n.m.r. spectrum.
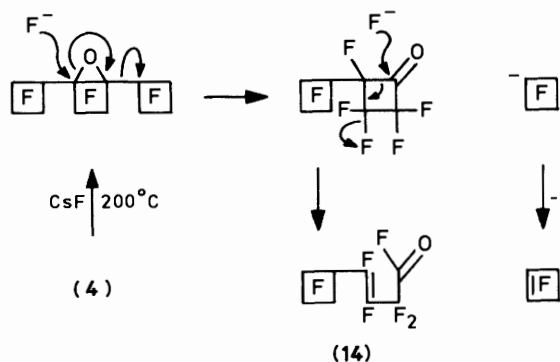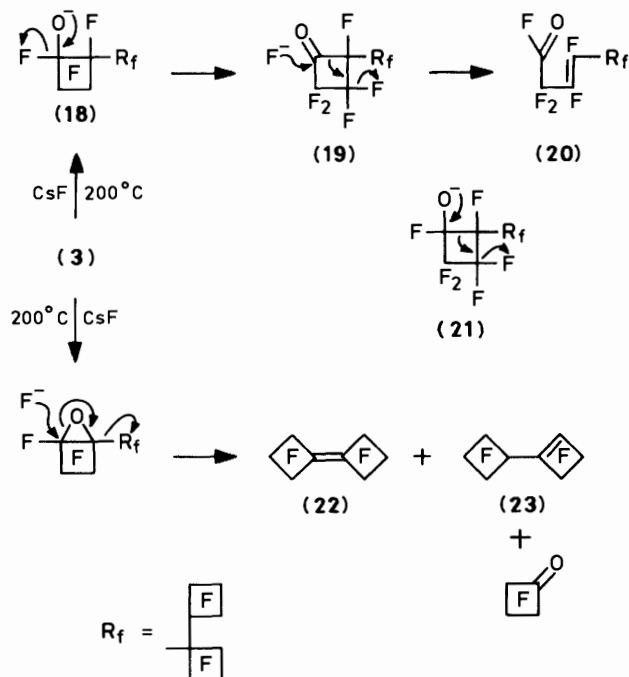
Scheme 3.

The unsymmetrical epoxides (2) and (3) both yielded mixtures of products derived from initial attack of F^- at both of the ring carbon atoms. In both cases attack occurred preferentially at the more substituted carbon, as found previously.[16] Thus the epoxide (2) yielded the ketone (16) as the major product (62%), and perfluorobutan-2-one (10%) and tetrafluoroethene as minor products from fragmentation of the intermediate (17) (Scheme 4). Similarly, the epoxide (3) afforded

Scheme 4.

Scheme 5.

the carbonyl fluoride (20) (60%), probably by attack of F^- on the intermediate cyclobutanone (19), although direct fragmentation (21) could also yield (20) (Scheme 5). The alkenes (22) and (23) were minor products (combined yield 15%) and their interconversion in the presence of fluoride ion has been reported.[21] Perfluorocyclobutanone, or more likely the acid fluoride, the complementary product to (22) and (23), was not observed.

The orientation of attack by fluoride ion on the epoxide (24) of hexafluoropropene has been a puzzle for many years. Attack occurs regiospecifically to give the intermediate oxyanion (25) exclusively, whereas intuitively we might anticipate the more branched oxyanion (26) to be preferred. These new results clearly indicate that there is a general preference for attack to occur so as to produce the oxyanion with most fluorine atoms attached to the carbon bearing the oxygen, e.g. (15) and (18). It now seems clear that the most important factor affecting these ring-opening reactions is the interaction of the atoms attached to the carbon atom at the oxyanion site, with the stability order being $-CF_2O^- > -CF(R_F)O^- > C(R_F)_2O^-$ (where R_F = perfluoroalkyl). This parallels the well-known order of C–F

bond strengths, $-CF_3 > -CF_2 > -CF$, and, furthermore, the relationship between interaction of oxygen atoms on a carbon centre and this series of CF bond strengths has been emphasised previously by Hine.[22] It is a small step then to assume that the stability of the oxyanions is in the same observed order for similar reasons.

Reaction of the epoxide (5) with fluoride ion gave a complex mixture of products. We had hoped to isolate a ring-expanded ketone, but the only product characterised was the carbonyl fluoride (29) (25%). Initial attack of fluoride ion at the position shown (Scheme 6), followed by opening of the cyclobutane ring gives the cyclononenone derivative (27). Further attack of F^- on (27) and ring opening is presumably encouraged by the high stability of the resulting tertiary carbanion (28). Loss of fluoride ion then gives alkene (29), with an exocyclic double bond, rather than the isomeric cyclobutene derivative; earlier work has shown there is a decisive chemical-shift difference between a fluorine attached to an endocyclic and an exocyclic double bond.[23]

It is noteworthy that we have isolated only acyclic ketones; the four- and nine-membered cyclic ketones react further with fluoride ion, although the last case is clearly not due to increased reactivity arising from ring strain. The acid fluorides are assigned structures (14), (20), and (29) rather than the isomeric α,β unsaturated ketone structures, which could arise by F^- induced migration of the double bond, on the basis of their u.v. spectra. All three acid fluorides, (14) (20), and (29), hydrolyse readily on exposure to air or moisture but products were not purified.
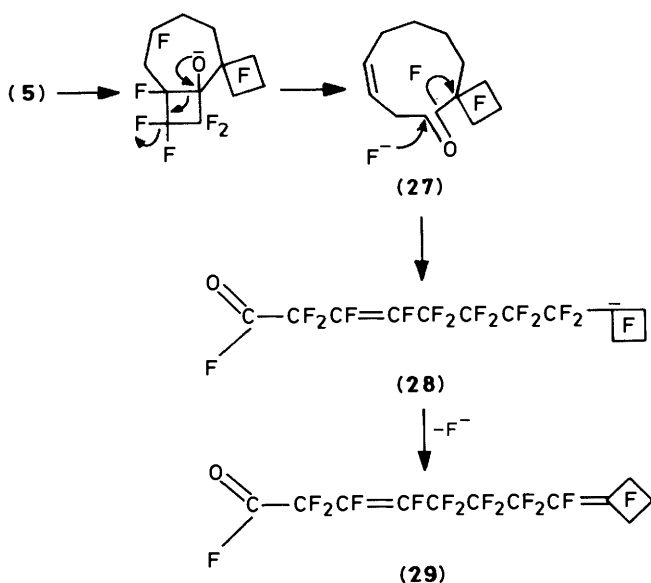
Scheme 6.

Experimental
Details of instrumentation and techniques have been described previously.[1]

General Procedure for Epoxidations.—A three-phase mixture of the fluorinated olefin, a 50% excess of sodium hypochlorite solution, and acetonitrile (a volume corresponding to 15% of the volume of the hypochlorite solution) was stirred at room temperature for 40 h. The fluorocarbon layer was separated, washed with water, dried ($MgSO_4$), and transferred to a cold trap. When necessary, further purification was achieved by distillation or preparative-scale g.l.c.

Epoxidation of Perfluoro-2,3-dimethylhex-3-ene (**7**).—The olefin (**7**) (33.0 g, 83 mmol), NaOCl solution (85 ml) and acetonitrile (15 ml) gave a liquid (27.0 g), b.p. 58—100 °C shown by g.l.c. to be a complex mixture of products. Preparative scale g.l.c. separated the following. (Z)-*Perfluoro-3,4-dimethyl-3,4-epoxyhexane,* (Z)-(**1**) (10.6 g, 31%) [Found: C, 23.0; F, 72.7%; M, 397 (M^+ − 19). $C_8F_{16}O$ requires C, 23.1; F, 73.1%; M, 416]; δ_F 66.0 and 79.3 (both 6 F, br, s), and 107.3 p.p.m. (4 F, br, d). (E)-*Perfluoro-3,4-dimethyl-3,4-epoxyhexane,* (E)-(**1**) (10.6 g, 31%) [Found: C, 23.2; F, 72.6%; M, 397 (M^+ − 19)]; δ_F 66.0 (6 F, m), 80.3 (6 F, h, J 6 Hz), and 108.3 p.p.m. (4 F, unsymmetrical m). (Z)-2H-*Perfluoro-(3-methyl-3,4-epoxypentane)* (Z)-(**6**) (4.4 g, 20%) (Found: C, 24.1; H, 0.3; F, 69.4%; M^+, 298. $C_6HF_{11}O$ requires C, 24.2; H, 0.3; F, 70.1%; M, 298); δ_F 69.3 (6 F, br, m), 84.3 (3 F, q, J 9 Hz), 122.6 (1 F, q, J 9 Hz), and 123.0 p.p.m. (1 F, q, J 9 Hz); δ_F 3.77 (q, J 4.3 Hz). (E)-2H-*Perfluoro-(3-methyl-2,3-epoxypentane),* (E)-(**6**) (1.8 g, 8%) (Found: C, 23.9; H, 0.2; F, 70.4%; M^+, 298); δ_F 69.3 (3 F, m), 75.2 (3 F, m), 84.3 (3 F, qq, J 5.6 Hz), and 117.0 p.p.m. (1 F, unsymmetrical m); δ_F 3.87 (q, J 5.3 Hz).

(E)- *and* (Z)-*Perfluoro-3-methyl-2,3-epoxypentane* (**2**).—The olefin (3.2 g, 10.5 mmol) as a mixture of (E)- (80%) and (Z)-(20%) isomers, NaOCl solution (30 ml), and acetonitrile (5 ml) yielded the epoxide (**2**), as an inseparable mixture of (E)-(73%) and (Z)-(27%) isomers (2.0 g, 60%) [Found: C, 23.1; F, 72.5%; M, 297 (M^+ − 19). $C_6F_{12}O$ requires C, 22.8; F, 72.2%; M, 316]; δ_F 68.7 (3 F, m), 76.7 (6 F, q, J 13 Hz, overlying m), 84.7 (6 F, m), 116.3 (4 F, m), and 149.3 (1 F, m), and 151.7 p.p.m. (1 F, q, J 22 Hz), consistent with reported n.m.r. data.[11b]

Perfluoro-1-(1'-cyclobutylcyclobutyl)-1,2-epoxycyclobutane (**3**).—The olefin (2.15 g, 4.4 mmol), NaOCl solution (20 ml), and acetonitrile (3 ml) gave the epoxide (**3**) (1.40 g, 62%) [Found: C, 28.6; F, 67.6%, M, 433 (M^+ − 69). $C_{12}F_{18}O$ requires C, 28.7; F, 68.1%, M, 502]; δ_F 112—135 (16 F), and 173.7 and 178.0 p.p.m. (each 1 F, br, s).

Perfluoro-1',2'-epoxytercyclobutane (**4**).—The olefin (3.2 g, 6.7 mmol), NaOCl solution (20 ml), and acetonitrile (10 ml) yielded the epoxide (**4**) (2.12 g, 64%) (Found: C, 28.8; F, 68.3%; M^+, 502. $C_{12}F_{18}O$ requires C, 28.7; F, 68.1%; M, 502); δ_F 118.9 and 127.9 (each 2 F, AB spectrum, J 203 Hz), 129.6 and 135.5 (each 2 F, AB spectrum, J 229 Hz), 128.1 and 133.5 (each 4 F, AB spectrum, J 229 Hz), and 183.7 p.p.m. (2 F, br, s).

Perfluoro-1,7-epoxyspiro(bicyclo[5.2.0]nonane-2,1'-cyclo-butane) (**5**).—The olefin (1.2 g, 2.5 mmol), NaOCl solution (6 ml), and acetonitrile (1 ml) gave the epoxide (**5**) (0.79 g, 64%) [Found: C, 28.0; F, 68.4%; M, 483 (M^+ − 19). $C_{12}F_{18}O$ requires C, 28.7; F, 68.1%; M, 502]; δ_F 109—137 p.p.m.

Reaction of the Epoxide (**6**) *with Sodium Methoxide.*—The epoxide (**6**) (1.50 g, 5.0 mmol) and an equimolar amount of sodium methoxide in the minimum amount of methanol was stirred at room temperature for 40 h. Volatile material was removed under reduced pressure and concentrated HCl (5 ml) was added to the solid residue. The fluorocarbon layer was removed and identified as an inseparable mixture of 1,1,1,4,4,5,5,5-*octafluoro-2-methoxy-3-trifluoromethylpentan-3-ol* (**11**), and 1,1,1,4,4,5,5,5-*octafluoro-3-methoxy-3-trifluoro-methylpentan-2-ol* (**12**) (combined yield 1.48 g, 89%) [Found: C, 25.8; H, 1.7; F, 63.1%; M, 291 (M^+ − 39). Calc. for $C_7H_5F_{11}O_2$: C, 25.5; H, 1.5; F, 63.3%; M, 330]; δ_F 71.0 and 73.0 (12 F, m), 80.3 (6 F, m), 117.7 (2 F, m), and 120.5 p.p.m. (2 F, br s); δ_H 4.40—3.93.

General Procedure for Reactions of Epoxides with Caesium Fluoride.—The epoxide and ca. 0.9 molar equivalents of caesium fluoride contained in a sealed tube were heated at 200 °C for 16 h. Volatile material was collected in a cold trap and, where necessary, further purified by preparative scale g.l.c.

Epoxide (**1**). The epoxide (**1**) (1.57 g, 3.8 mmol) and CsF (0.50 g, 3.3 mmol) yielded volatile material (1.44 g) which was transferred from the cold trap into an n.m.r. tube which was sealed *in vacuo*. The [19]F n.m.r. spectrum showed that the product consisted of perfluorobut-2-ene and perfluorobutan-2-one by comparison with literature values.[24]

Epoxide (**2**). The epoxide (**2**) (3.16 g, 10 mmol) and CsF (1.36 g, 9 mmol) yielded volatile material (2.98 g) from which perfluorobutan-2-one was separated and identified as above. The major product, a volatile liquid, could not be obtained pure, but was identified as perfluoro-3-methylpentan-2-one (**16**) (1.96 g, 62%) (Found C, 21.4; F, 70.0%; M^+, 316. Calc. for $C_6F_{12}O$: C, 22.8; F, 72.2%; M, 316); δ_F 71.1, 80.0, and 83.4 (each 3 F, m), 119.0 (CF_2, m), and 180.1 (1 F, m); $\nu_{max.}$ 1 855 cm^{-1} (C=O).

Epoxide (**3**). The epoxide (**3**) (2.07 g, 4.12 mmol) and CsF (0.53 g, 3.5 mmol) yielded a volatile liquid (1.86 g). Vacuum transfer separated the olefins (**22**) and (**23**) (combined yield 0.20 g, 15%) identified by comparison of g.c., i.r., and [19]F n.m.r. data with authentic samples. The residue consisted of one major component identified as the *carbonyl fluoride* (**20**) (1.20 g. 58%) (Found: C, 29.0; F, 68.4%; M^+, 502. $C_{12}F_{18}O$ requires C, 28.7; F, 68.1%; M, 502); δ_F −18.5 (1 F, s, COF), 109—135 (16 F), and 177.6 p.p.m. (1 F, s); $\nu_{max.}$ 1 885 cm^{-1} (C=O); $\lambda_{max.}$ 276 nm.

Epoxide (**4**). The epoxide (**4**) (2.00 g, 4.1 mmol) and CsF (0.56 g, 3.7 mmol) yielded a product (1.9 g) consisting of perfluorocyclobutene, which was collected in a flexible gas reservoir and identified by comparison of its i.r. spectrum with

that of authentic material, and the *carbonyl fluoride* (14) as a colourless liquid purified by preparative scale g.l.c. (0.74 g, 55%) (Found: C, 27.9; F, 67.5%; M^+, 340. $C_8F_{12}O$ requires C, 28.2; F, 67.5%; M, 340); δ_F −18.3 (1 F, s, COF), 117—136 (10 F), and 176.1 p.p.m. (1 F, s); $\nu_{max.}$ 1 885 cm^{-1} (C=O); $\lambda_{max.}$ 278 nm.

Epoxide (5). The epoxide (5) (2.50 g, 5.0 mmol) and CsF (0.70 g, 5.0 mmol) gave a brown oil shown by g.l.c. to be a complex mixture of products, only one of which was identified. Vacuum transfer separated the *carbonyl fluoride* (29) (0.45 g, 18%) (Found: C, 28.2; F, 68.6%; M^+, 502. $C_{12}F_{18}O$ requires C, 28.7; F, 68.1%; M, 502); δ_F −20.5 (1 F, s, COF) and 120—141 p.p.m. (17 F); $\nu_{max.}$ 1 885 cm^{-1} (C=O); $\lambda_{max.}$ 280 nm.

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