Highly Selective Ring-opening of 1,3,3-Trihalogenoepoxycyclohexanes by Boron Trihalides; Methodology for the Determination of the Regioselectivity in the Cyclisation of 2,2,6,6-Tetrahalogenocyclohexanols†

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Reaction of 1,3,3-trihalogeno-7-oxabicyclo[4.1.0]heptanes with boron trihalides (F, Cl, Br) resulted in the regio- and stereo-selective formation in high yield of the corresponding tetrahalohydrins. In these reactions the hypervalent halogenoborate species are responsible for the selective halogenation of the epoxides by *cis* opening. A methodology is given to predict the regioselectivity in the epoxidic cyclisation of 2,2,6,6-tetrahalogenocyclohexanols. These processes allowed the preparation of all the isomers of 1,3,3-trihalogeno-7-oxabicyclo[4.1.0]heptanes or 2,2,6,6-tetrahalogenocyclohexanols (X = Cl, F), very useful intermediates.

As the introduction of fluorine into organic molecules becomes increasingly important,[1] so too does the search for selective, efficient and simple fluorinating methods. In this connection much interest has been shown in the ring-opening of epoxides to afford fluorohydrins.[2] The use of anhydrous hydrogen fluoride in such work is dangerous, requiring extreme caution because of its high toxicity. In addition, because of its high reactivity it often affords polymers[3] or rearrangement products. Thus, various reagents[4] such as KF, KHF_2, KHF_2–AlF_3, Bu_4NF, $Bu_4N^+\cdot H_2F_3$, $Bu_4PF\cdot(HF)_n$ (n = 0, 1 and 2), $(Pr^iO)_2TiF_2$ or SiF_4, various amine·HF adducts[5] such as pyridine polyhydrofluoride (HF·pyridine), $Et_3N\cdot 3HF$, $Pr^i_2NH\cdot 3HF$ *etc.* have been used successfully as alternatives and these reagents can have different selectivities with the same oxirane. In a similar way to hydrogen fluoride or its modified forms as fluorine sources, the Lewis acid boron trifluoride–diethyl ether complex ($BF_3\cdot OEt_2$) can split epoxide rings nucleophilically, a vicinal fluorohydrin forming during the subsequent hydrolysis. So far, this reaction, used only in a few instances,[6] and then mainly in steroid chemistry,[7] has been proved to be rather unselective and to exhibit a pronounced solvent dependence. In a preliminary communication[8] we have described the ring-opening of 1,3,3-

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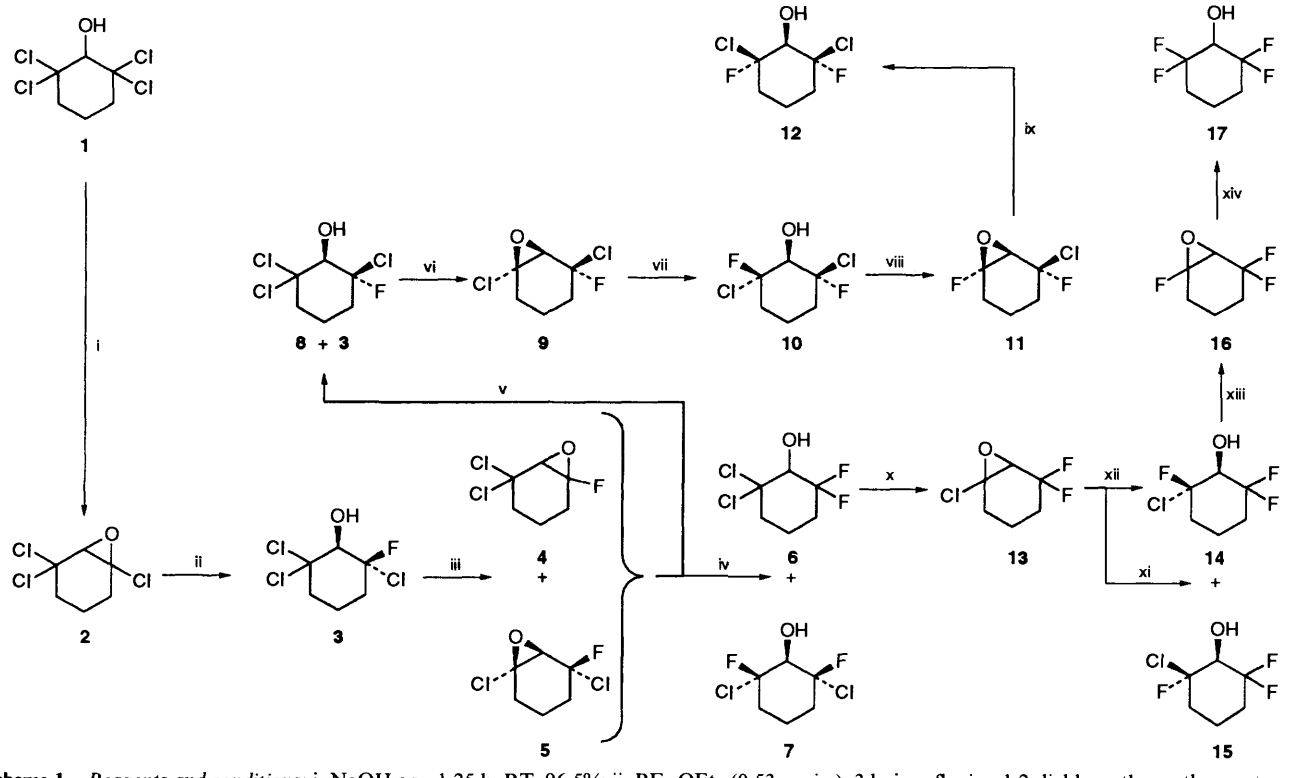


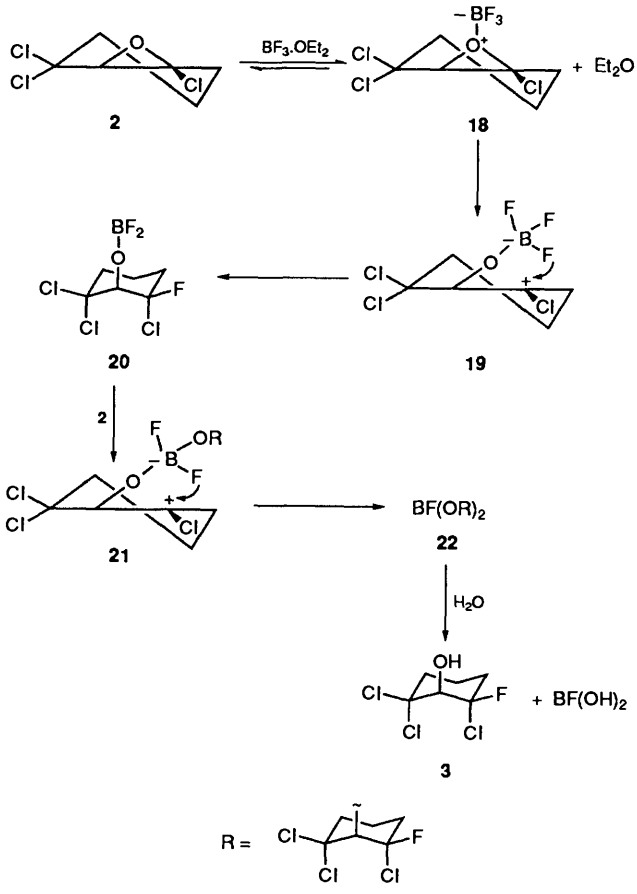
Scheme 1 *Reagents and conditions:* i, NaOH aq., 1.25 h, RT, 96.5%; ii, $BF_3\cdot OEt_2$ (0.53 equiv.), 3 h, in refluxing 1,2-dichloroethane, then water at 80 °C, 92%; iii, NaOH aq., 1.25 h, RT, 96%, **4**:**5** = 93:7 (^1H and ^{19}F NMR); iv, $BF_3\cdot OEt_2$ (0.53 equiv.), in refluxing 1,2-dichloroethane, 1.75 h then water, **6**:**7** = 93:7 (GC), total yield 82%; v, BCl_3 (0.55 equiv.), 4 °C then 1 h at RT, CH_2Cl_2, **8**:**3** = 93:7 (GC), total yields 85.5%, **8** isolated 74%; vi, NaOH aq., 1.25 h, RT, 96%; vii $BF_3\cdot OEt_2$ (0.55 equiv.), in refluxing 1,2-dichloroethane, 1.75 h then water, 98%; viii, NaOH aq., 1.25 h, RT, 81%; ix, BCl_3 (0.55 equiv.), 4 °C then 1 h at RT, CH_2Cl_2, 60%; x, NaOH aq., 1.25 h, RT, 87%; xi, HF·pyr., 1 h 20 min, 0 °C then RT, **14**:**15** = 83:17 (isolated products), total yield 83.5%; xii, $BF_3\cdot OEt_2$ (0.55 equiv.), in refluxing 1,2-dichloroethane, 1.5 h then water, **14**, 82.5%; xiii, NaOH aq., 1.25 h, RT, 82%; xiv, HF·pyr., THF, 1 h 10 min, 0 °C then at RT, 49% or $BF_3\cdot OEt_2$ (0.55 equiv.), in refluxing 1,2-dichloroethane, 5 h then water, 60%

trihalogeno-7-oxabicyclo[4.1.0]heptanes* (X = Cl, F) with BF_3·OEt_2 which afforded the corresponding *cis*-fluorohydrins in high yield and selectivity (better than the Olah's reagent HF·pyridine[9]). From the readily available 2,2,6,6-tetrachlorocyclohexanol **1**,[10] in addition to the iterative preparation of 2,2,6,6-tetrafluorocyclohexanol **17** by a succession of cyclisations followed by ring-opening reactions by BF_3·OEt_2[8], we have now demonstrated that boron trichloride reacts in a similar way to BF_3·OEt_2 allowing the preparation of all the diastereoisomeric tetrahalogeno alcohols (Cl, F) bearing from one to three atoms of fluorine (Scheme 1). The regio- and stereo-selectivities in the ring-opening of the α-halogeno epoxides have also been extended to boron tribromide (BBr_3).

Thus, treatment of 2,2,6,6-tetrachlorocyclohexanol **1** with aqueous NaOH[11] at room temperature afforded a very thermally stable 1,3,3-trihalogeno-7-oxabicyclo[4.1.0]heptane **2** in 96% yield.† This epoxide with BF_3·OEt_2 (0.53 equiv.) in refluxing 1,2-dichloroethane gave regio- and stereo-selectively, upon hydrolysis and purification by column chromatography, the corresponding *cis*-fluorohydrin **3** in higher yield than with HF·pyridine. The *cis*-configuration‡ was established by spectroscopic methods ($^3J_{HF}$ 18.4 Hz) and finally confirmed by synthesis of the *trans* isomer **8** by an alternative route (Scheme 1).

The proposed mechanism of the nucleophilic fluorination of the epoxide **2** (Scheme 2) would be, in a first step *via* an equilibrium, a boron complexation of the Lewis acid BF_3·Et_2O with a lone pair on the epoxidic oxygen to give the complex **18**. Then the complex **18**, through an axial cleavage, would be converted into a zwitterionic trifluoroborate **19** followed by an intramolecular transfer of fluoride to the primary carbocationic centre (stabilised by the chlorine atom) to lead exclusively to a *cis*-adduct, the difluoroborate **20**. The intermediate **20** would have sufficient Lewis acid character to be complexed with a further molecule of the α-chloro epoxide **2** and would yield, *via* a similar intramolecular transfer of fluoride from the zwitterionic difluoroborate **21**, the monofluoroborate **22**. Upon hydrolysis the latter monofluoroborate would give the *cis*-fluorohydrin **3**. This mechanism was in good agreement with the regio- and stereo-chemical courses of the reaction as well as the fact that the reaction was realized with only 0.53 equiv. of BF_3·OEt_2.§ Moreover, the ^{1}H NMR spectrum (80 MHz) of a $CDCl_3$ solution of a partially hydrolysed reaction mixture allowed the observation of a doublet at 4.89 ppm ($^3J_{H,F}$ 19.2 Hz) assigned to 1-H of the monofluoroborate **22**. The fluoroborates are known to be difficult to hydrolyse sometimes, in our case several hours after the addition of D_2O at room temperature in the NMR tube, the doublet at 4.89 ppm had disappeared whereas the signals (doublet at 4.04 ppm) for 1-H of the fluorohydrin **3** had increased; this indicated that hydrolysis was completed.

Treatment of the fluorohydrin **3** with aqueous NaOH, under the same conditions as specified previously, led in a very regioselective manner to the α-fluoro epoxide **4** mixed with a little of its regioisomer **5** [ratio **4**:**5** = 93:7 (Scheme 1)]. Use of KOH in ethanol or aqueous LiOH at room temperature



Scheme 2 Mechanism of ring-opening of the α-chloro epoxide **2** by BF_3·OEt_2

produced a similar ratio of the two regioisomers **4** and **5**. Only the departure of the chlorine atom was observed, and that mainly from the chloro-fluoro carbon group, first, because of the need for anticoplanarity of the hydroxy group and the leaving substituent (*vide infra* rule i) and second as a result of the mesomeric assistance given by the fluorine atom (*vide infra* rule iii). It was not possible to separate the two regioisomers **4** and **5** by classical techniques, so introduction of the second fluorine by BF_3·OEt_2 was directly carried out on the mixture **4**:**5**. This led to a mixture of the 2,2-difluoro alcohol **6** and its regioisomer **7** in the same ratio 93:7 (GC determination) as the starting material, demonstrating for the respective substrates the expected regio- and stereo-selectivities. At this stage, the two fluorohydrins **6** and **7** could be separated by column chromatography.

During the ring-opening of the 1,3,3-trihalogeno-7-oxabicyclo[4.1.0]heptanes **2** and **4** with BF_3·OEt_2, the observed regio- and diastereo-selectivities clearly indicated that the attack of a fluoride ion took place exclusively with *cis*-stereoselectivity, on the more substituted carbon. We expected that the use of BCl_3 would give the same selectivities in the chlorination of the epoxide **4**,‡ leading to the *trans*-fluorohydrin **8**.

Thus, treatment of a mixture of the regioisomeric epoxides **4**:**5** in the ratio 93:7 (^{1}H NMR determination) with BCl_3 (0.55 equiv.) in dichloromethane gave a mixture of the regioisomeric *trans*- and *cis*-fluorohydrins **8**:**3** in the same ratio as the starting material 93:7 (GC determination). Moreover, the two diastereoisomers **8** and **3** could be separated by column chromatography and the *trans*-fluorohydrin **8** was obtained in 74% yield. The structure of the *trans*-fluorohydrin **8** was assigned on the basis of its coupling constant value: $^3J_{H,F}$ 7.6 Hz

* To our knowledge, action of boron trifluoride etherate on α-chlorooxiranes has been only reported to give rearrangement products but not to lead to *gem*-chlorofluoroalcohols.[13]

† Unlike most α-chlorooxiranes, the oxirane **2** was particularly stable and can be distilled under reduced pressure without thermal rearrangement.

‡ In all cases *cis* refers to the position of the introduced halogen atom compared to the hydroxy group.

§ Using 0.33 equiv. BF_3·OEt_2 led in our conditions to an incomplete formation of the *cis*-fluorohydrin **3**.

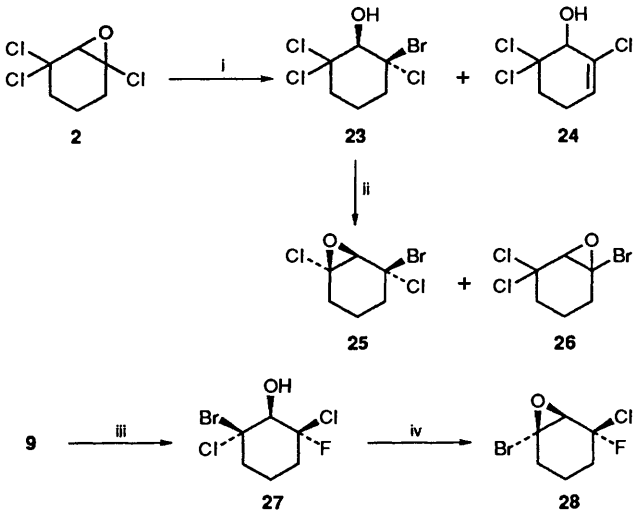
against 18.4 Hz for the *cis*-fluorohydrin **3**. Thus, from the *cis*-fluorohydrin **3** a two-step cyclisation and chlorination procedure induced by BCl_3 gave the diastereoisomeric *trans*-fluorohydrin **8**, corresponding to an inversion of the secondary alcohol. This compound was not directly available by Mitsunobu's reaction,[12] probably because of steric hindrance in the fluorohydrin **3**. The subsequent cyclisation of the *trans*-fluorohydrin **8** by aqueous NaOH afforded, both totally regioselectively and quantitatively, the α-chloro epoxide **9**; this was because the chlorine atom was a better leaving group than the fluorine atom (*vide infra* rule ii). Introduction of a second fluorine into the epoxide **9** with BF_3·OEt_2 led regio- and stereoselectively to the 2,6-difluoro alcohol **10** (98%). Its *meso* diastereoisomer **12** has been prepared by regioselective ring-closure of the alcohol **10** to give the α-fluoro epoxide **11** followed by chlorination of the latter using BCl_3 (Scheme 1).

Treatment of the 2,2-dichloro-6,6-difluorocyclohexanol **6** (Scheme 1) with aqueous NaOH afforded the corresponding α-chloro epoxide **13** (87%), departure of the chlorine being similar to that observed for the alcohol **8**. Introduction of a third fluorine atom into the oxirane **13** was totally diastereoselective with BF_3·OEt_2 and yielded the *trans*-chlorohydrin **14** (82.5%); with HF·pyridine a mixture of the same *trans*-chlorohydrin **14** and its diastereoisomer, the *cis*-chlorohydrin **15** (ratio **14**:**15** = 83:17 ratio of isolated products) was obtained and separated by column chromatography. Finally, cyclisation of the alcohol **14** with aqueous NaOH gave the 1,3,3-trifluoro-1,2-epoxycyclohexane **16** in 82% yield. A final fluorination with HF·pyridine in tetrahydrofuran gave the expected 2,2,6,6-tetrafluorocyclohexanol **17** (49%); BF_3·OEt_2 gave an improved yield of the alcohol **17** (up to 60%) demonstrating the superiority of such a reagent with this type of epoxide. For a direct preparation of the 2,2,6,6-tetrafluorocyclohexanol **17** separation of the regioisomers **6** and **7** was unnecessary since the cyclisation–fluorination sequence used led exclusively to the *trans*-chlorohydrin **14**. Thus, after final purification by column chromatography the tetrafluorohydrin **17** was prepared in eight steps from the chlorinated analogue **1** in a 25% overall yield.

In a manner similar to that used to introduce selectively a fluorine or a chlorine atom with BF_3·OEt_2 or BCl_3, respectively, treatment with boron tribromide of 1,3,3-trihalogeno-7-oxabicyclo[4.1.0]heptanes **2** and **9** afforded regio- and stereo-selectively the corresponding 2,2,6,6-tetrahalogenocyclohexanols **23** and **27** *via* a *cis*-opening of the epoxide ring (Scheme 3). Ring-opening of the trichloro epoxide **2** by BBr_3 yielded a mixture of the *cis*-bromohydrin **23** and the allylic alcohol **24** (elimination product) in the ratio **23**:**24** = 83:17 (^{1}H NMR determination); direct cyclisation of the mixture afforded the regioisomeric epoxides **25** (structures assigned by ^{13}C NMR spectroscopy) and **26** in the ratio **25**:**26** = 97:3 (GC determination). In the latter reaction, the allylic alcohol **24** stayed in the basic aqueous layer after extraction with diethyl ether.

The epoxide **9** underwent *cis*-bromination by BBr_3 in dichloromethane to give 2-bromo-2,6-dichloro-6-fluorocyclohexanol **27** in good yield. Subsequent cyclisation of this afforded regioselectively 1-bromo-3-chloro-3-fluoro-7-oxabicyclo-[4.1.0]heptane **28** in 80% yield (Scheme 3).

Whichever boron trihalide was used the selectivity was similar, with *cis*-opening of the 1,3,3-trihalogeno-7-oxabicyclo[4.1.0]heptanes and good yields of product. Moreover, the ring-closure by aqueous NaOH of all the 2,2,6,6-tetrahalogenocyclohexanols to give the corresponding 1,3,3-trihalogeno-7-oxabicyclo[4.1.0]heptanes was generally extremely regioselective under our conditions. From our results the structure of the corresponding α-halogeno epoxides can be predicted from the following three rules, given in order of priority. (i) The leaving halogen atom is, in all cases, *anti* to the hydroxy group



Scheme 3 *Reagents and conditions:* i, BBr_3 (0.55 equiv.), CH_2Cl_2, 0 °C then RT, 2.5 h, **23**:**24** = 83:17, 85% total yield; ii, NaOH aq., 1.25 h, RT, **25**:**26** = 97:3 (GC and ^{1}H NMR), 72.5%; iii, BBr_3 (0.55 equiv.), CH_2Cl_2, 4 °C then RT, 1.5 h, 73%; iv, NaOH aq., 1.25 h, RT, 80%

as a result of an anticoplanar transition state for the epoxidic cyclisation. (ii) If two different halogens are both in an *anti* situation, that which is the greater nucleofuge (Cl > F) will be exclusively substituted. (iii) If two identical halogens are in an *anti* situation with respect to the hydroxy group, the intramolecular substitution will take place predominantly on that carbon affected by the higher mesomeric effect (F > Cl > Br). Examples are given to illustrate these rules. Use of the rules i and ii: the alcohols **8**, **10**, **14** and **27** gave exclusively and, respectively, the epoxides **9**, **11**, **16** and **28**. Use of the rules i and iii: the alcohols **3** and **23** gave predominantly and, respectively, the epoxides **4** and **25**.

In brief, the use of 0.53–0.55 equiv. of BX_3 (X = F, Cl, Br) in nucleophilic ring-opening of 1,3,3-trihalogeno-7-oxabicyclo-[4.1.0]heptanes followed by the regioselective intramolecular cyclisation of the 2,2,6,6-tetrahalogenocyclohexanols so formed, produced an iterative process of regio- and stereo-controlled halogeno substitution. This process allowed the preparation of previously unknown halogeno epoxides or alcohols, bearing three mixed halogen atoms. The difficult inversion of a highly hindered *cis*-fluorohydrin **3** to a *trans*-fluorohydrin **9** in good yield *via* a two step procedure has been possible. The regio- and stereo-controlled α-halogeno epoxides and tetrahalohydrins prepared are important intermediates,[8] the chemical properties of which are being studied.

Experimental

General.—M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 16-PC IR-FT spectrophotometer as pure liquid films or as solutions in $CDCl_3$. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC200 (at 200 or 80 MHz) or AW80 (at 50 or 20 MHz) instruments, respectively, with tetramethylsilane as internal standard. ^{19}F NMR spectra were recorded on an AC200 (190 MHz) with fluorotrichloromethane as internal standard. *J* Values are given in Hz. Mass spectra were recorded on a JEOL JMS AX 500 mass spectrometer using electron impact (EI) or chemical ionisation (CI) modes. GC analyses were performed on a Hewlett-Packard 5890 gas chromatograph equipped with a H-P.-5.1 column [16 ft 1/50 in (i.d.)]. Flash-column chromatography was performed with Merck Kieselgel 60 (230–400 mesh ASTM) support. Ether refers to diethyl ether and light

petroleum refers to fraction with b.p. 40–60 °C. TLC analyses were performed on glass plates (Merck silica gel 60 F_{254}) and spots were visualised by UV illumination and then heating with phosphomolybdic acid. Microanalyses were performed by INSA laboratories, Rouen.

Reagents and Solvents.—Reactions requiring anhydrous conditions were carried out under a static argon atmosphere using oven dried glassware. All solvents were purified and dried using standard methods. After extraction the combined organic layers were dried over $MgSO_4$. Solvents were removed under reduced pressure by rotary evaporation.

Polyethylene flasks and syringes were used for experiments with HF·pyridine and normal glassware was used for experiments with BF_3·OEt_2.

2,2,6,6-*Tetrachlorocyclohexanol* **1**.—(i) *By reduction with sodium borohydride.* To a solution of 2,2,6,6-tetrachlorocyclohexanone (7.08 g, 30 mmol) in anhydrous ether (120 cm^3) was added portionwise sodium borohydride (0.57 g, 15 mmol) and dropwise methanol (11 cm^3). The reaction mixture was stirred at room temperature for 1 h and then quenched with water (12 cm^3) at 4 °C. After being stirred for a further 15 min, the mixture was extracted with ether (× 5) and the combined layers were dried, filtered and evaporated to give the pure alcohol **1** (7.11 g, 100%).

(ii) *By reduction with isopropylmagnesium chloride.* To a solution of 2,2,6,6-tetrachlorocyclohexanone (1.91 g, 8.09 mmol) in anhydrous THF (12 cm^3) was added dropwise at −55 °C isopropylmagnesium chloride (1.25 mol dm^{-3} in ether; 8 cm^3, 10.0 mmol). The reaction mixture was stirred for 1 h, cooled at −50 °C and then quenched with 5% aqueous NH_4Cl (10 cm^3). The mixture was extracted with ether and the combined organic layers were dried and evaporated to yield the crude alcohol **1** which was recrystallised from pentane (1.73 g, 90%), m.p. 58 °C (Found: C, 30.3; H, 3.3. Calc. for $C_6H_7Cl_4O$: C, 30.28; H, 3.39%); ν_{max}(Nujol)/cm^{-1} 3470 (OH); δ_H(200 MHz; $CDCl_3$) 1.50–2.85 (6 H, m, 3-H, 4-H, 5-H), 3.15 (1 H exchangeable, s, 1-OH) and 4.10 (1 H, s, 1-H); δ_C(50 MHz; DMSO) 20.4 (4-C), 44.9 (3-C and 5-C), 81.2 (1-C) and 93.0 (2-C and 6-C).

General Procedure for Preparation of Epoxides.—NaOH pellets were added portionwise to a suspension of the alcohol in water at 10–15 °C. The reaction mixture was stirred at room temperature for 1.25 h after which it was diluted with ether and stirred for 5 min; it was then extracted with ether (× 4). The combined organic layers were dried, filtered and concentrated under reduced pressure. Specific conditions are given for each product.

1,3,3-*Trichloro*-7-*oxabicyclo*[4.1.0]*heptane* **2**. From the alcohol **1** (15.2 g, 53.8 mmol) in water (70 cm^3) and NaOH (21 g, 0.525 mol) was obtained the epoxide **2** (12.42 g, 96.5%) as a colourless liquid, of purity >96% from GC analysis. The epoxide **2** could be distilled (b.p. 40 °C/0.1 mmHg, 92%), b.p. 213 °C (Found: C, 35.8; H, 3.6. $C_6H_7Cl_3O$ requires C, 35.77; H, 3.50%); ν_{max}(neat)/cm^{-1} 1130 and 1080; δ_H(200 MHz; $CDCl_3$) 1.25–2.00 (2 H, m, 5-H), 2.00–2.80 (4 H, m, 4-H and 6-H) and 3.80 (1 H, s, 2-H); δ_C(50 MHz; $CDCl_3$) 18.7 (5-C), 31.7 (6-C), 38.8 (4-C), 65.7 (2-C), 78.5 (1-C) and 84.5 (3-C); *m/z* (30 eV, EI) 169, 167, 165 (M^+ − Cl, 8, 43, 64%), 137 (13), 129 (9), 126 (8), 124 (40), 122 (60), 112 (29), 111 (21), 110 (42), 103 (32), 101 (85), 93 (51), 91 (100), 87 (14), 77 (16), 75 (44), 74 (40), 73 (14), 67 (13), 65 (75), 63 (43), 59 (57), 58 (20) and 55 (24).

3,3-*Dichloro*-1-*fluoro*-7-*oxabicyclo*[4.1.0]*heptane* **4**. From the alcohol **3** (2 g, 9.03 mmol) in water (12 cm^3) and NaOH (1.5 g, 37.5 mmol) were obtained the epoxide **4** with its regioisomer **5** in the ratio (determined from ^1H and ^{19}F NMR) **4**:**5** = 93:7 (1.61 g, 96% total yield) (Found: C, 39.0; H, 3.8. $C_6H_7Cl_3FO$ requires C, 38.95; H, 3.81%); ν_{max}(neat)/cm^{-1} 1180 and 1085; δ_H(200 MHz; $CDCl_3$) 1.38–2.47 (6 H, m, 4-H, 5-H, 6-H) and 3.88 (1 H, d, *J* 1.8, 2-H); δ_C(50 MHz; C_6D_6) 17.6 (d, *J* 8.4, 5-C), 24.3 (d, *J* 25.9, 6-C), 39.2 (4-C), 63.1 (d, *J* 10.5, 2-C), 85.0 (3-C) and 96.5 (d, *J* 277.2, 1-C); δ_F(190 MHz; $CDCl_3$) −119.5 (s, 0.97F).

1,3-*Dichloro*-3-*fluoro*-7-*oxabicyclo*[4.1.0]*heptane* **9**. The alcohol **8** (1.60 g, 7.22 mmol) was treated in water (22 cm^3) with NaOH (0.85 g, 21.3 mmol) to give the epoxide **9** (1.28 g, 96%) as a colourless liquid, (purity >98% from GC analysis) (Found: C, 38.8; H, 3.8. $C_6H_7Cl_2FO$ requires C, 38.95; H, 3.81%); ν_{max}(neat)/cm^{-1} 1410, 1130, 1110, 1090 and 1080; δ_H(200 MHz; $CDCl_3$) 1.10–2.80 (6 H, m, 3-H, 4-H and 5-H) and 3.69 (1 H, d, *J* 4.3, 2-H); *m/z* (30 eV, EI) 151, 149 (M^+ − Cl, 17, 55%), 124 (8), 122 (15), 121 (9), 120 (8), 112 (30), 110 (45), 109 (8), 108 (13), 107 (13), 106 (39), 103 (8), 101 (24), 93 (34), 91 (33), 86 (9), 85 (63), 75 (100), 65 (27), 59 (29) and 55 (21).

3-*Chloro*-1,3-*difluoro*-7-*oxabicyclo*[4.1.0]*heptane* **11**. The alcohol **10** (0.18 g, 0.88 mmol) was treated in water (3 cm^3) with NaOH (0.12 g, 3 mmol) to give the epoxide **11** (0.13 g, 81%) as a colourless liquid, (purity >98% from GC analysis); ν_{max}(neat)/cm^{-1} 1450, 1420, 1360, 1340, 1180, 1170, 1100 and 1080; δ_H(200 MHz; $CDCl_3$) 1.40–2.50 (6 H, m, 4-H, 5-H and 6-H) and 3.73 (1 H, t, *J* 2.4, 2-H).

1-*Chloro*-3,3-*difluoro*-7-*oxabicyclo*[4.1.0]*heptane* **13**. The alcohol **6** (0.60 g, 2.93 mmol) was treated in water (5 cm^3) with NaOH (0.48 g, 12.0 mmol) to give the epoxide **13** (0.43 g, 87%) as a colourless liquid (Found: C, 43.4; H, 4.2. $C_6H_7ClF_2O$ requires C, 42.75; H, 4.19%); ν_{max}(neat)/cm^{-1} 1120, 1100, 975 and 835; δ_H(200 MHz; $CDCl_3$) 1.32–2.79 (6 H, m, 4-H, 5-H and 6-H) and 3.56 (1 H, t, *J* 2.2, 2-H); δ_C(50 MHz; C_6D_6) 16.7 (t, *J* 10), 29.6 (t, *J* 23), 32.4, 59.2 (t, *J* 40), 65.8 and 120.1 (t, *J* 236).

1,3,3-*Trifluoro*-7-*oxabicyclo*[4.1.0]*heptane* **16**. The alcohol **14** (1 g, 5.3 mmol) in water (10 cm^3) was treated with NaOH (800 mg, 20.0 mmol) to give (careful evaporation at RT) the epoxide **16** (660 mg, 82%) as a colourless liquid (Found: C, 47.6; H, 4.4. $C_6H_7F_3O$ requires C, 47.38; H, 4.64%); ν_{max}(neat)/cm^{-1} 1460, 1370, 1250, 1240 and 1210; δ_H(200 MHz; $CDCl_3$) 1.50–2.00 (4 H, m), 2.10–2.40 (2 H, m) and 3.60 (1 H, q, *J* 1.9, 2-H); δ_C(50 MHz; $CDCl_3$) 15.9 (m, 5-C), 24.8 (d, *J* 26.0, 6-C), 19.4 (t, *J* 23.7, 4-C), 56.0 (m, 2-C), 94.7 (d, *J* 270.6, 1-C) and 119.0 (t, *J* 242.8, 3-C); δ_F(190 MHz; $CDCl_3$) −128.0 (1 F, s, 1-F), −101.2 (1 F, t, *J* 15.3, 3-F) and −100.9 (1 F, t, *J* 12.3, 3-F); *m/z* (200 eV, IC, isobutane) 153(100), 133(20) and 113(22) (Found: M^+, 152.0392. Calc. for $C_6H_7F_3O$: *M*, 152.0449).

3-*Bromo*-1,3-*dichloro*-7-*oxabicyclo*[4.1.0]*heptane* **25**. The mixture of alcohols **23** and **24** (ratio **23**:**24** = 80:20; 0.71 g, containing 2.1 mmol of alcohol **23**) in water (56 cm^3) was treated with NaOH (0.60 g, 15.0 mmol) to give, after work-up (the alcohol **24** was retained in the aqueous layer during extraction), followed by flash-column chromatography with ether–light petroleum (5:95) as eluent, a mixture of the epoxides **25** and **26** (0.36 g, 72.5% total yield) as a colourless liquid in the ratio **25**:**26** = 97:3 (determined by GC and ^1H NMR analysis). The epoxides **25** and **26** (Found: C, 29.4; H, 2.9. $C_6H_7BrCl_2O$ requires C, 29.30; H, 2.87%); ν_{max}(neat)/cm^{-1} 1439, 1401, 1336, 1283, 1186 and 1080; δ_H(200 MHz; $CDCl_3$) 1.40–1.67 (1 H, m), 1.69–1.93 (1 H, m), 2.20–2.65 (4 H, m) and 3.90 (1 H, s, 2-H); δ_C(50 MHz; $CDCl_3$) 18.8 (s, 5-C), 31.8 (s, 6-C), 40.5 (s, 4-C), 66.6 (s, 2-C), 73.0 (s, 1-C) and 79.5 (s, 3-C); *m/z* (200 eV, IC, NH_3) 165 (100), (M + H − HBr), 146 (22), 129 (10), 118 (18), 104 (30), 92 (26), 82 (62), 75 (10) and 63 (3). 1-Bromo-3,3-dichloro-7-oxabicyclo[4.1.0]heptane **26**; δ_C(50 MHz; $CDCl_3$) 19.3 (s, 5-C), 34.1 (s, 6-C), 38.8 (s, 4-C), 65.7 (s, 2-C), 69.5 (1-C) and 84.3 (s, 3-C).

1-*Bromo*-3-*chloro*-3-*fluoro*-7-*oxabicyclo*[4.1.0]*heptane* **28**. The alcohol **9** (0.2 g, 0.75 mmol) in water (3 cm^3) was treated

with NaOH (0.12 g, 3.0 mmol) to give the epoxide **28** (0.15 g, 80%) as a colourless liquid (purity >97.5% from GC analysis) (Found: C, 32.1; H, 3.5. $C_6H_7BrClFO$ requires C, 31.40; H, 3.07%); ν_{max}(neat)/cm^{-1} 1410, 1335, 1240 and 1070; δ_H(200 MHz; $CDCl_3$) 1.40–2.90 (6 H, m, 4-H, 5-H and 6-H) and 3.75 (1 H, d, *J* 4.2, 2-H).

General Procedure for Fluorination.—(i) *By* HF·*pyridine.* HF·pyridine, introduced into a polyethylene flask with a polyethylene syringe, was stirred whilst epoxide was added to it with a syringe pump. Stirring was continued for the appropriate time after which the mixture was poured into ice–water and extracted (×4) with dichloromethane. The combined organic layers were dried, filtered and evaporated to dryness and the crude alcohol was purified by flash-column chromatography. Specific conditions are given for each product.

(ii) *By* BF_3·OEt_2. BF_3·OEt_2 (0.53–0.55 equiv.) was added *via* a syringe to a solution of the epoxide in 1,2-dichloroethane in normal glassware and the mixture was refluxed and then hydrolysed with water or hydrochloric acid (6 mol dm^{-3}). After extraction with dichloromethane (×4), the combined extracts were dried, filtered and concentrated under reduced pressure. The crude alcohol was purified by flash-column chromatography. Specific conditions are given for each product.

2,2,6-*Trichloro*-6-*fluorocyclohexanol* **3**.—(i) *By* HF·*pyridine.* To HF·pyridine (3.2 cm^3) was added the epoxide **2** (1.93 g, 9.6 mmol) during 25 min at −35 °C and the reaction mixture was stirred for 3 h at this temperature; it was then gradually warmed to room temperature over 30 min. Work-up gave a crude oil containing a mixture of the alcohols **3** and **24** (2.03 g) (ratio **3**:**24** = 85:15 by ^{1}H NMR). Since the alcohols **3** and **24** were not separable by flash-column chromatography or distillation, the alcohol **3** was separated chemically; thus, morpholine (1 cm^3, 11.5 mmol) was added dropwise at RT to the crude mixture (2.03 g) in ether (10 cm^3). Stirring was continued for 15 min after which the solvent was evaporated. The residual solid was washed with light petroleum (3 × 10 cm^3) and dried. To the morpholinium salt (2.31 g, 82.5%) in ether (75 cm^3) was added dropwise at 10 °C HCl (1.2 mol dm^{-3}; 20 cm^3). The reaction mixture was stirred for 15 min and then extracted with ether (4 × 15 cm^3), dried and evaporated to give the alcohol **3** (1.7 g, 82.5%). *Morpholinium salt*, m.p. 67–68 °C (Found: C, 38.8; H, 5.4; N, 4.4. $C_{10}H_{17}Cl_3FNO_2$ requires C, 38.92; H, 5.55; N, 4.54%); δ_H(80 MHz; $CDCl_3$) 1.48–2.97 (10 H, m), 3.50–3.78 (4 H, m and 2 H exchangeable, s) and 3.99 (1 H, d, *J* 19.7); δ_C(20 MHz; C_6D_6) 19.8, 39.8 (d, *J* 21.8), 45.0, 50.0, 67.5, 81.6 (d, *J* 18.6) and 113.1 (d, *J* 19.7).

(ii) *By* BF_3·OEt_2. BF_3·OEt_2 (0.325 cm^3, 0.53 equiv.) was added to a solution of the epoxide **2** (1.0 g, 4.96 mmol) in 1,2-dichloroethane (7 cm^3) and the reaction mixture was refluxed for 3 h. Work-up and flash-column chromatography with ether–light petroleum (10:90) as eluent gave the alcohol **3** (1.01 g, 92%), m.p. 37–38 °C (Found: C, 32.6; H, 3.5. $C_6H_8Cl_3FO$ requires C, 32.54; H, 3.64%); ν_{max}($CDCl_3$)/cm^{-1} 3570 (OH); δ_H(80 MHz; $CDCl_3$) 1.49–2.96 (6 H, m, 3-H, 4-H and 5-H), 3.14 (1 H exchangeable, d, *J* 9.6, 1-OH) and 4.04 (1 H, dd, *J* 18.4, *J* 9.6, 1-H); δ_C(20 MHz; C_6D_6) 19.6 (s, 4-C), 39.5 (d, *J* 22.3, 5-C), 44.6 (s, 3-C), 81.2 (d, *J* 19.0, 1-C), 91.6 (d, *J* 1.9, 2-C) and 112.4 (d, *J* 254.5, 6-C); δ_F(190 MHz; $CDCl_3$) −123.05 (1 F, s).

2,2-*Dichloro*-6,6-*difluorocyclohexanol* **6**.—(i) *By* HF·*pyridine.* To HF·pyridine (2.75 cm^3) was added in 20 min at 0 °C a mixture of the epoxides **4** and **5** (ratio **4**:**5** = 93:7) (1.53 g, 8.27 mmol). After 10 min, the reaction mixture was allowed to warm to RT at which it was stirred for 50 min. Water (10 cm^3) was added at −10 °C to the mixture which was then worked up to provide a residue which was subjected to flash-column chromatography with ether–light petroleum (4:96) as eluent to afford the alcohol **6** (1.2 g, 71%) and a mixture of the alcohols **6** and **7** (ratio **6**:**7** = 82:18) (12%). A similar reaction with a mixture of the epoxides **4** and **5** (ratio **4**:**5** = 93:7) (10 g, 54.0 mmol) gave, after 3 iterative cycles of flash-column chromatography using the foregoing eluent, the alcohol **7** (200 mg, 0.97 mmol) purity >98.5% (GC analysis).

(ii) *By* BF_3·OEt_2. BF_3·OEt_2 (0.26 cm^3, 0.55 equiv.) was added to a solution of the epoxides **4** and **5** in (**4**:**5** = 93 : 7) in 1,2-dichloroethane (10 cm^3). The mixture was refluxed for 1.75 h after which work-up followed by flash-column chromatography with ether–light petroleum (10:90) as eluent afforded a mixture of the alcohols **6** and **7** (ratio **6**:**7** = 93:7 determined by GC analysis) (82% total yield).

The alcohol **6** (Found: C, 34.9; H, 3.9. $C_6H_8Cl_2F_2O$ requires C, 35.15; H, 3.93%); ν_{max}($CDCl$)/cm^{-1} 3550–3450 (OH); δ_H(200 MHz; $CDCl_3$) 1.60–1.80 (6 H, m, 3-H, 4-H and 5-H), 3.14 (1 H exchangeable, s, 1-OH) and 3.99 (1 H, dd, *J* 15.95, *J* 6.4, 1-H); δ_C(20 MHz; C_6D_6) 18.6 (d, *J* 7.2, 4-C), 31.5 (t, *J* 23.0, 5-C), 43.0 (3-C), 78.0 (d, *J* 25.6, 1-C), 90.6 (s, 2-C) and 120.0 (t, *J* 247.7, 6-C); δ_F(190 MHz; $CDCl_3$) −97.9 (1 F, d, *J* 245.2) and −111.4 (1 F, d, *J* 245.7); *m*/*z* (30 eV, EI) 208, 206, 204 (M^+, 1, 10, 15%), 190, 188, 186 (2, 12, 28), 171 (4), 169 (12), 156 (17), 154 (26), 153 (18), 151 (19), 149 (16), 124 (61), 122 (100), 120 (18), 110 (18), 109 (17), 93 (20), 91 (48), 85 (41), 77 (32), 75 (74), 65 (23), 59 (16) and 51 (16).

2,6-*Dichloro*-2,6-*difluorocyclohexanol* **7**, m.p. 80–81 °C (Found: C, 35.0; H, 3.8. $C_6H_8Cl_2F_2O$ requires C, 35.15; H, 3.93%); ν_{max}($CDCl_3$)/cm^{-1} 3450 (OH); δ_H(200 MHz; $CDCl_3$) 1.45–2.85 (6 H, m, 3-H, 4-H and 5-H), 2.93 (1 H exchangeable, d, *J* 9.6, 1-OH) and 3.93 (1 H, dt, *J* 20.6, *J* 9.6, 1-H); δ_C(50 MHz; $CDCl_3$) 18.6 (4-C), 39.5 (t, *J* 11.3, 3-C and 5-C), 79.5 (d, *J* 19.7, 2-C and 6-C) and 111.6 (d, *J* 254.3, 1-C); *m*/*z* (30 eV, EI) 208, 206, 204 (M^+, 1, 6, 9%), 190, 188, 186 (0.4, 4, 6), 170, 168 (8, 26), 139 (11), 133 (15), 121 (13), 120 (18), 113 (15), 106 (17), 105 (11), 104 (47), 96 (12), 94 (15), 93 (34), 91 (31), 88 (12), 85 (54), 75 (100), 67 (10), 65 (21) and 59 (41).

2,6-*Dichloro*-2,6-*difluorocyclohexanol* **10**.—BF_3·OEt_2 (0.47 cm^3, 0.55 equiv.) was added to a solution of the epoxide **9** (1.89 g, 7.03 mmol) in 1,2-dichloroethane (20 cm^3) and the mixture was refluxed for 1.75 h. Work-up followed by flash-column chromatography with ether–light petroleum (10:90) as eluent afforded the alcohol **10** (1.43 g, 98%) of purity >97% (from GC analysis) (Found: C, 35.5; H, 4.0. $C_6H_8Cl_2F_2O$ requires C, 35.15; H, 3.93%); ν_{max}(neat)/cm^{-1} 3530–3420 (OH); δ_H(200 MHz; $CDCl_3$) 1.40–2.90 (6 H, m, 3-H, 4-H and 5-H), 3.07 (1 H exchangeable, d, *J* 8.5, 1-OH) and 4.07 (1 H, dt, *J* 8.3, 8.5, 1-H); δ_F(190 MHz; $CDCl_3$) −99.7 (1 F, s) and −119.1 (1 F, s); *m*/*z* (30 eV, EI) 208, 206, 204, (M^+, 1, 3, 5%), 190, 188, 186 (0.4, 3, 4), 170, 168 (7, 21), 139 (11), 138 (20), 137 (28), 133 (14), 129 (10), 122 (10), 121 (15), 120 (25), 113 (16), 106, 104 (18, 53), 96 (11), 94 (16), 93 (30), 91 (31), 88 (17), 85 (65), 75 (100), 65 (21) and 59 (34).

2-*Chloro*-2,2,6-*trifluorocyclohexanol* **14**.—(i) *By* HF·*pyridine.* To HF·pyridine (3 cm^3) was added in 25 min at 0 °C the epoxide **13** (1.23 g, 7.30 mmol). After 10 min, the reaction mixture was warmed to RT and stirred for 1 h 20 min. Work-up and purification by flash-column chromatography with ether–light petroleum (10:90 to 12:88) as eluent gave the alcohol **14** (0.16 g), a mixture of alcohols **14** and **15** (0.80 g) (ratio **14**:**15** = 95:5 determined by GC analysis) and the alcohol **15** (0.19 g) (83.5% total yield).

(ii) *By* BF_3·OEt_2. BF_3·OEt_2 (0.16 cm^3, 0.55 equiv.) was added to a solution of the epoxide **13** (0.39 g, 2.31 mmol) in 1,2-dichloroethane (33 cm^3) and the mixture was refluxed for 1.5 h. Work-up followed by flash-column chromatography with ether–light petroleum (10:90) as eluent afforded the alcohol **14**

(0.36 g, 82.5%), m.p. 42–43 °C (Found: C, 38.2; H, 4.3. $C_6H_8ClF_3O$ requires C, 38.30; H, 4.11%); ν_{max}(neat)/cm^{-1} 3400 (OH); δ_H(200 MHz; $CDCl_3$) 1.50–2.80 (6 H, m, 3-H, 4-H and 5-H), 3.10 (1 H exchangeable, s, 1-OH) and 3.98 (1 H, dt, *J* 16.6, 5.1, 1-H); δ_C(50 MHz; C_6D_6) 17.5 (s, 4-C), 31.4 (t, *J* 22.0, 5-C), 37.6 (d, *J* 22.0, 3-C), 75.8 (q, 1-C), 94.6 (d, *J* 246.6, 2-C) and 120.9 (t, *J* 246.6, 6-C).

2-*Chloro-2,2,6-trifluorocyclohexanol* **15**, ν_{max}(neat)/cm^{-1} 3440 (OH); δ_H(200 MHz; $CDCl_3$) 1.53–2.65 (6 H, m, 3-H, 4-H and 5-H), 2.75 (1 H exchangeable, *J* 6.0, 1-OH) and 3.78–4.22 (1 H, m, 1-H); δ_C(50 MHz; $CDCl_3$) 17.5 (t, *J* 4.9, 4-C), 29.4 (t, *J* 23.1, 5-C), 36.0 (d, *J* 19.5, 3-C), 73.9 (q, 1-C), 114.7 (d, *J* 246.6, 2-C) and 122.7(t, *J* 232.8, 6-C); *m/z* (70 eV, EI) 188, 190, (M^+, 5, 16%), 170, 168 (5, 8), 153 (20), 133 (7), 121 (6), 113 (23), 106 (30), 75 (100), 59 (84) and 45 (52) (Found: M^+, 188.0218. Calc. for $C_6H_8ClF_3O$: *M*, 188.0216).

2,2,6,6-*Tetrafluorocyclohexanol* **17**.—(i) *By* HF·*pyridine*. To HF·pyridine (0.3 cm^3, 0.59 mmol) was added in 10 min at 0 °C a solution of the epoxide **16** (0.09 g, 0.59 mmol) in THF (0.1 cm^3). The reaction mixture was stirred at RT for 1 h 10 min after which it was treated with water (3 cm^3) at 0 °C. Work-up and purification by flash-column chromatography with ether–light petroleum (30:70) as eluent gave the alcohol **17** (0.05 g, 49%).

(ii) *By* BF_3·OEt_2. BF_3·OEt_2 (0.23 cm^3, 0.53 equiv.) was added to a solution of the epoxide **13** (0.5 g, 3.29 mmol) in 1,2-dichloroethane (5 cm^3). The mixture was refluxed for 5 h. Work-up followed by flash-column chromatography with ether–light petroleum (10:90) as eluent afforded the alcohol **17** (0.34 g, 60%), m.p. 65–66 °C (Found: C, 41.6; H, 4.7. $C_6H_8F_4O$ requires C, 41.87; H, 4.68%); ν_{max}(neat)/cm^{-1} 3590 (OH); δ_H(200 MHz; $CDCl_3$) 1.63–2.18 (6 H, m, 3-H, 4-H and 5-H), 2.53 (1 H exchangeable, d, *J* 6.6, 1-OH) and 3.80–4.50 (1 H, m, 1-H); δ_C(50 MHz; $CDCl_3$) 16.2 (t, *J* 4.6, 4-C), 30.0 (q, *J* 11.3, 3-C and 5-C), 71.7 (q, *J* 25.9, 1-C) and 120.9 (t, *J* 246.7, 2-C and 6-C); δ_F(190 MHz; $CDCl_3$) −110.5 (2 F, d, *J* 253.8, 6-CF_2) and −105.2 (2 F, d, *J* 250.6, 2-CF_2); *m/z* (70 eV, EI) 172 (16), 152 (18), 113 (16), 104 (19), 90 (36), 88 (25), 85 (21), 80 (22), 77 (54), 75 (100) and 71 (4) (Found: M^+, 172.0483. Calc. for $C_6H_8OF_4$: *M*, 172.0511).

General Procedure for Chlorination (BCl_3) *or Bromination* (BBr_3).—To a solution of the epoxide in dichloromethane was added at 4 °C BX_3 (X = Cl or Br) (1 mol dm^{-3} in dichloromethane; 0.55 equiv.) *via* a syringe. The reaction mixture was warmed to RT, stirred for the specified time and then hydrolysed at −10 °C with water. After extraction with dichloromethane (× 4), the combined extracts were dried, filtered and evaporated. The crude alcohol was purified by flash-column chromatography. Specific conditions are given for each product.

2-*Bromo*-2,6-*dichloro*-6-*fluorocyclohexanol* **27**. To a solution of the epoxide **9** (0.98 g, 5.3 mmol) in dichloromethane (6.5 cm^3) was added BBr_3 (2.91 cm^3, 2.91 mmol). The reaction mixture was stirred at RT for 1.5 h. Work-up and purification by flash-column chromatography with ether–light petroleum (5:95) as eluent gave the alcohol **28** (1.03 g, 73%) (purity > 97% from GC analysis) (Found: C, 27.0; H, 2.9. $C_6H_8BrCl_2FO$ requires C, 27.10; H, 3.03%); ν_{max}(neat)/cm^{-1} 3495 (OH); δ_H(200 MHz; $CDCl_3$) 1.50–3.00 (6 H, m, 3-H, 4-H and 5-H), 3.17 (1 d, 1 H exchangeable, *J* 6.3, 1-OH) and 4.05 (t, 1 H, *J* 6.3, 1-H); *m/z* (200 eV, IC, NH_3) 301 (98, $[M + N_2H_7]^+$), 284 (100, $[M + NH_4^+]$), 268 (2), 221 (4), 201 (8), 184 (24), 166 (6), 148 (14), 127 (4), 110 (4), 93 (6), 82 (12), 73 (12) and 69 (6).

2-*Bromo*-2,6,6-*trichlorocyclohexanol* **23**. To a solution of the epoxide **2** (1.69 g, 8.4 mmol) in dichloromethane (10 cm^3) was added BBr_3 (4.61 cm^3, 4.61 mmol). The reaction mixture was stirred at RT for 2.5 h. Work-up gave a mixture of the alcohols **23** and **24** (ratio **23**:**24** = 83:17 determined by GC analysis) (85% total yield). Flash chromatography gave mixtures of the alcohols **23** and **24** in the following ratios: 86:14 (1.01 g), 80:20 (0.71 g) and 75:25 (0.37 g).

2,2,6-*Trichloro*-6-*fluorocyclohexanol* **8**. To a solution of the epoxides **4** and **5** (ratio **4**:**5** = 93:7) (12.12 g, 65.5 mmol) in dichloromethane (80 cm^3) was added BCl_3 (36 cm^3, 36 mmol). The reaction mixture was stirred for 1 h after which it was treated with water (75 cm^3). Work-up provided a crude product containing the alcohols **8** and **3** (ratio **8**:**3** = 93:7 determined by GC analysis). Purification by flash-column chromatography with ether–light petroleum (4:96) as eluent gave first the pure alcohol **8** (10.73 g, 74%) as a colourless oil and a mixture of the alcohols **8** and **3** (ratio **8**:**3** = 90:10) (1.65 g, 11%). The alcohol **8** (Found: C, 32.6; H, 3.7. $C_6H_8Cl_3FO$ requires C, 32.53; H, 3.64%); ν_{max}(neat)/cm^{-1} 3510 (OH); δ_H(200 MHz; $CDCl_3$) 1.67–2.86 (6 H, m, 3-H, 4-H and 5-H), 3.10 (1 H exchangeable, d, *J* 7.6, 1-OH) and 4.12 (1 H, t, *J* 7.6, 1-H); δ_C(50 MHz; $CDCl_3$) 19.4 (d, *J* 5.6, 4-C), 37.4 (d, *J* 20.4, 5-C), 42.5 (s, 3-C), 79.2 (d, *J* 24.7, 1-C), 90.3 (d, *J* 6.1, 2-C) and 113.7 (d, *J* 248.6, 6-C); δ_F(190 MHz; $CDCl_3$) −98 (1 F, s); *m/z* (30 eV, EI) 226, 224, 222, 220 (M^+, 0.4, 3, 8, 8%), 208, 206, 204, 202 (0.4, 3, 10, 11), 188, 186, 184 (5, 25, 39), 156 (23), 155 (23), 154 (36), 153 (33), 149 (19), 124 (18), 122 (50), 120 (81), 112 (24), 110 (35), 109 (17), 106 (15), 101 (33), 93 (49), 91 (100), 85 (41), 75 (86), 65 (31) and 59 (18).

2,6-*Dichloro*-2,6-*difluorocyclohexanol* **12**. To a solution of the epoxide **11** (0.11 g, 0.65 mmol) in dichloromethane (3 cm^3) was added BCl_3 (0.36 cm^3, 0.55 equiv.). The reaction mixture was stirred for 1 h after which water (3 cm^3) was added to it. Work-up and purification by flash-column chromatography with ether–light petroleum (5:95) as eluent gave the alcohol **12** (0.08 g, 60%) as a colourless oil (purity > 95% from GC analysis); δ_H(200 MHz; $CDCl_3$) 1.35–2.70 (6 H, m, 3-H, 4-H and 5-H), 2.82 (1 H exchangeable, d, *J* 5.0, 1-OH) and 4.08 (1 H, q, *J* 5.0, 1-H).

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