Free radical chemistry. Part 11.[1] Additions of cyclic and acyclic alcohols and diols to hexafluoropropene

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Peroxide and γ-ray initiated reactions of cyclic alcohols, and various cyclic and acyclic diols, with hexafluoropropene are described. Regiospecific additions are observed and structures follow from NMR data. X-Ray crystallography established the structures of some isomers. A variety of polyfluoroalkylated alkenes, dienes and aromatic building-blocks were derived from the polyfluoroalkylated alcohols.

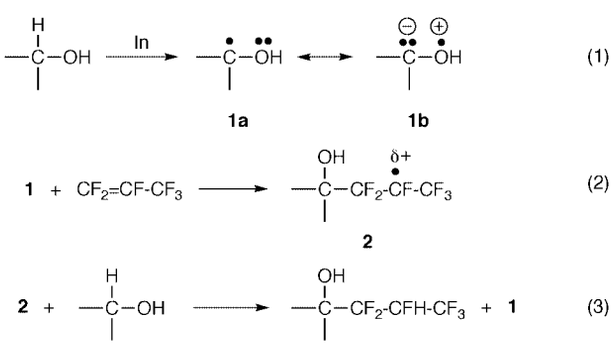
Introduction

There is considerable interest, world-wide, in the development of methodology for the introduction of groups containing fluorine into organic compounds because of the profound effects on the physical, chemical and biological properties that such groups can induce. This is illustrated by the fact that perfluoroalkylated compounds continue to find many uses in the pharmaceutical and plant protection industries, while high performance surfactants and textile treatment agents utilise perfluoroalkylated systems.[2] Existing processes for the preparation of polyfluoroalkylated compounds include the conversion of functional groups (*e.g.* carbonyl to difluoromethylene[3,4]) and the transfer of fluorocarbon groups as nucleophiles,[5] electrophiles[6] or free-radicals.[7] Methodology for the introduction of trifluoromethyl groups into organic substrates has been extensively studied,[8–10] especially for the synthesis of various pharmaceuticals and plant protection agents.

In this series, we are pursuing an interest in the use of the carbon–hydrogen bond as a functional group for the introduction of fluorinated groups into organic compounds and materials *via* free-radical addition reactions to unsaturated fluorocarbons. It is useful to emphasise that very high-yielding preparative processes have been reported,[11] which avoid the use of highly toxic initiators such as organo-tin hydrides and here we develop further this approach to carbon–carbon bond formation through additions of cyclic alcohols to hexafluoropropene (HFP). Free-radical additions of alcohols to various fluorinated alkenes have been described previously[12] but, surprisingly, additions of cyclic alcohols to HFP have not been reported and, indeed, earlier attempts to effect such reactions were described as unsuccessful.[13] We have also explored reactions of both acyclic and cyclic diols with HFP and we are aware of only one report of radical addition of a diol to HFP (low yield).[14]

Results and discussion

HFP is an extremely electrophilic alkene derivative that will react with a wide range of nucleophiles[12] and, furthermore, this fluorinated alkene is very susceptible to radical attack, especially by 'nucleophilic' radicals.[15,16] A particular merit of using HFP in free radical addition reactions is that polymerisation or formation of telomers do not normally compete, probably due to steric effects arising from the trifluoromethyl group. Of course it is well known that alcohols form radicals readily, especially at sites attached to oxygen, and that the stabilising interaction of a radical centre with oxygen **1a** renders the radical nucleophilic in character **1b**, as depicted in eqn. (1), Scheme 1. Thus, in principle, we have a very favourable system [eqns. (2) and (3)], and it is probable that, until



Scheme 1

recently,[17] the importance of polar characteristics of radicals in synthetic procedures has been underestimated, although the significance in this field, *i.e.* reactions of fluorinated alkenes, has been emphasised previously.[11,15,16]

Indeed, we now find that a range of cyclic alcohols **3**–**8** react with HFP in highly efficient processes, to yield the adducts **9**–**14** as indicated in Table 1. Initiation was effected by γ-rays at room temperature and, in some examples, di-*tert*-butyl peroxide at 140 °C. It is useful to note that there was little discernible difference in either the overall yields or in the site selectivity of the reaction with the type of initiation process used. In each case, for carbocyclic rings up to and including cycloheptanol, radical addition occurred selectively at the carbon with the attached hydroxy. Only in the case of cyclooctanol **7** did the product also contain a small amount of a component arising from attack at a site in the alcohol which is removed from the tertiary carbon. The additions proceed by the well-known free-radical chain process outlined in eqns. (1)–(3) (Scheme 1).

We emphasised above the significance of polar effects on the addition step, eqn. (2), but such effects are also important in the hydrogen abstraction step, eqn. (3). At this stage, we now have

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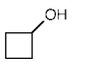
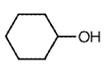
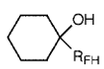
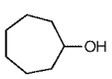
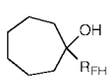
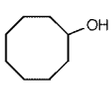
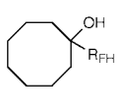
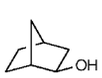
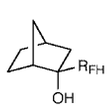
Table 1 Free radical additions of cyclic alcohols to hexafluoropropene

Substrate	Conditions (A or B)[a] HFP : substrate	Monoadduct yield (%)[b]	Diadducts yield (%)[c]
 **3**	A, 1.15 : 1	 **9** (78)	Trace
 **4**	A, 1.14 : 1	 **10** (72)	Trace
	B, 1.07 : 1	**10** (65)	6
 **5**	A, 1.18 : 1	 **11** (76)	Trace
	B, 1.10 : 1	**11** (65)	5
 **6**	A, 1.18 : 1	 **12** (68)	Trace
 **7**	A, 1.15 : 1	 **13** (18)	**15** 40
 **8**	A, 1.18 : 1	 **14** (54)	11

[a] A = γ-rays, rt, 10 d; B = Di-*tert*-butyl peroxide, 140 °C, 24 h. [b] Isolated yield. $R_{FH} = -CF_2CFHCF_3$. [c] Isolated yield of mixtures of diastereoisomers.

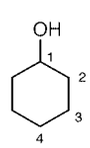


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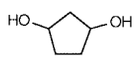
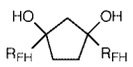
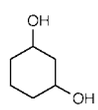
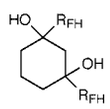
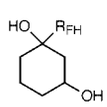
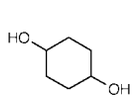
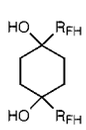
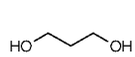
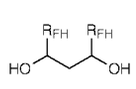
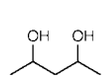
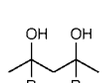
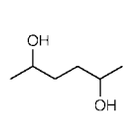
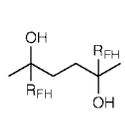
Fig. 1

an extremely *electrophilic* radical **2** which abstracts a hydrogen atom from the relatively electron-rich alcohol and, to understand fully the high site selectivities indicated in Table 1, we need to appreciate the fact that the oxygen atom is responsible for *two* effects. The first is that described above, which *promotes* and influences the addition step, eqns. (1) and (2), but, secondly, the oxygen is also inductively electron withdrawing and will therefore reduce reactivity towards attack by the radical at other positions, where the conjugative stabilisation **1a**,**1b** is not applicable. Thus site 1 in cyclohexanol **5** (Fig. 1) is clearly activated towards hydrogen abstraction by **2**, but the other sites 2–4 are *deactivated* by inductive electron withdrawal by the oxygen atom.

The deactivation is also enhanced by introduction of a polyfluorinated alkyl group, and this is sufficient to determine that the mono-addition products are the principal components of the reaction mixtures, even when a slight excess of HFP is used, Table 1. However, some di- and poly-addition products are often observed in amounts that are increased with the level of excess HFP, as well as the duration of reaction. The larger amount of product **15**, corresponding to di-addition, obtained from cyclooctanol **7** reflects the fact that there are methylene sites that are now sufficiently far removed from the alcohol functionality to enable reaction to occur. Thus we observed much less site selectivity in favour of the tertiary C–H. *exo*-

Table 2 Free radical additions of cyclic and acyclic diols to hexafluoropropene

Substrate	Conditions (A or B)[a] HFP : substrate	Adducts yield (%)[b]
 **16**	2.36 : 1	 **23** (63)
 **17**	2.25 : 1	no reaction
 **18**	2.27 : 1	 **24** (45)  **29** (30)
 **19**	2.27 : 1	 **25** (83)
 **20**	4.60 : 1	 **26** (42)
 **21**	2.36 : 1	 **27** (75)
 **22**	2.34 : 1	 **28** (34)

[a] A = γ-rays, rt, 10 d; B = Di-*tert*-butyl peroxide, 140 °C, 24 h. [b] Isolated yield. $R_{FH} = -CF_2CFHCF_3$.

Norborneol (*exo*-bicyclo[2.2.1]heptan-2-ol) reacted selectively but slowly, and we attribute this to steric crowding around the hydroxy carbon. We are unable, at this stage, to determine the structures of the di- and poly-adducts referred to in Table 1, because of the complexity of the spectra of these systems.

In spite of the fact that there is only one report of addition of diols to HFP[14] we now find that additions of various diols proceed smoothly, and examples of additions of both cyclic and acyclic systems are shown in Table 2. Cyclohexane-1,2-diol **17** did not yield significant amounts of useful product, whereas cyclohexane-1,3-diol **18** gave both mono- and di-adducts **29** and **24** and cyclohexane-1,4-diol **19** gave good conversion to the di-adduct **25**.

Clearly, free-radical additions to diols are governed by the same factors that affect the cyclic alcohols outlined above leading to site-specific polyfluoroalkylated products. However, it is clear that when the hydroxy groups are at adjacent positions, as in cyclohexane-1,2-diol **17**, both alcohol centres are deactivated by σ-electron withdrawal by oxygen.

Characterisation

The orientation of radical additions to HFP is well established, with radical attack generally occurring principally at the difluoromethylene site,[12] except in situations where the attacking

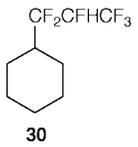


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Fig. 2

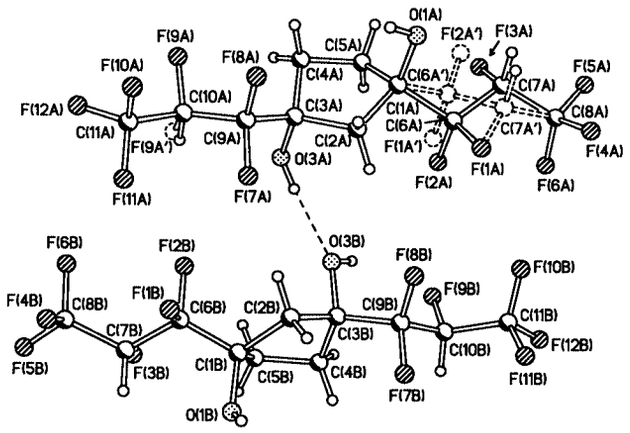


Fig. 3 Two independent molecules (A and B) of *trans*-**23** in crystal. Minor positions of disordered atoms have primed numbers.

radical is electrophilic in character. We have emphasised above that radicals derived from alcohols are, indeed, quite nucleophilic **1b** and, consistent with this fact, *only* products arising from attack at difluoromethylene are observed, to the limits of detection by ^{19}F NMR. The structure of the side-chains, CF_2CFHCF_3, followed simply from the ^{19}F NMR spectra and assignment of sites of substitution in the alcohols also followed from the various ^{13}C NMR data. ^{13}C NMR chemical shifts for CH_3 and CH_2 sites in the alcohols occur in the region 20–40 ppm, while the carbons attached to hydroxy groups have shifts to significantly lower frequency in the region 60–80 ppm. The shift induced by introduction of the polyfluoroalkyl group is much smaller than this difference, for example the ^{13}C NMR shifts for the ring system **30**, Fig. 2, still occur in the region 20–40 ppm.

Consequently, in all of the products shown in Tables 1 and 2, assignment of the resonance arising from the carbon atom(s) attached to hydroxy in the ^{13}C NMR spectra is unambiguous. Furthermore, these signals are triplets and show clear two-bond $^2J_{CF}$ couplings of *ca.* 25 Hz.[18] An interesting observation in these cyclic systems, *e.g.* **11**, is the fact that the ring carbon atoms are each magnetically inequivalent, *i.e.* six separate signals are observed, due to the presence of the stereogenic centre in the polyfluoroalkyl side-chain.[19]

The complexity of the NMR spectra of the di-adducts, which are obtained as mixtures of diastereoisomers, precludes firm assignments of stereochemistry. However, we were able to obtain crystal structures of components that crystallised preferentially from solutions of **23** or **24** in dichloromethane, and these are shown in Figs. 3 and 4. In the case of **24**, derived from cyclohexane-1,3-diol, the polyfluoroalkyl groups are situated in the equatorial positions and the hydroxy groups indicate an interaction through hydrogen bonding. Similarly, in the case of **23**, synthesised from cyclopentane-1,3-diol, the polyfluoroalkyl groups are adopting pseudo-equatorial positions and, in each case, the polyfluoroalkyl groups take up configurations that tend to minimise interaction, reminiscent of the structure of poly-tetrafluoroethylene.

Chemistry of polyfluoroalkyl alcohol derivatives

We were interested in pursuing the chemistry of the polyfluoroalkylated alcohol adducts synthesised above with the aim of developing general routes for the preparation of a variety of

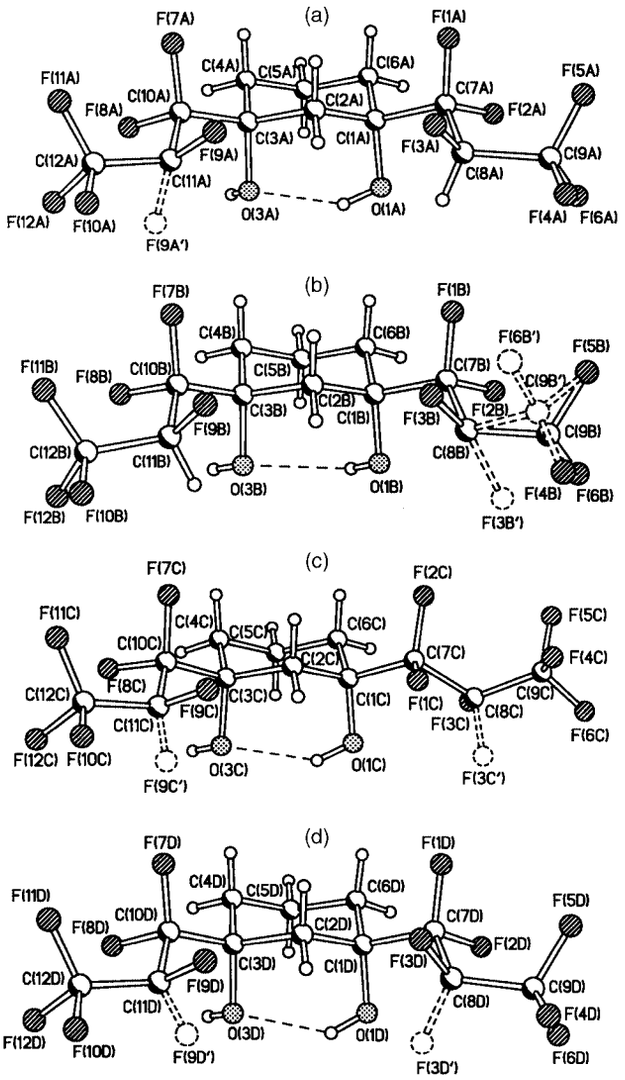


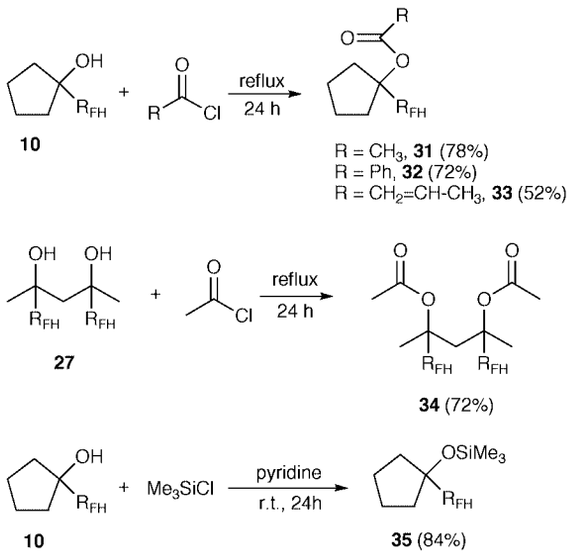
Fig. 4 Four independent molecules of *cis*-**24** in crystal. Minor positions of disordered atoms have primed numbers.

fluorine-containing 'building blocks' which could, in principle, be used for further synthetic manipulation to more structurally sophisticated systems.

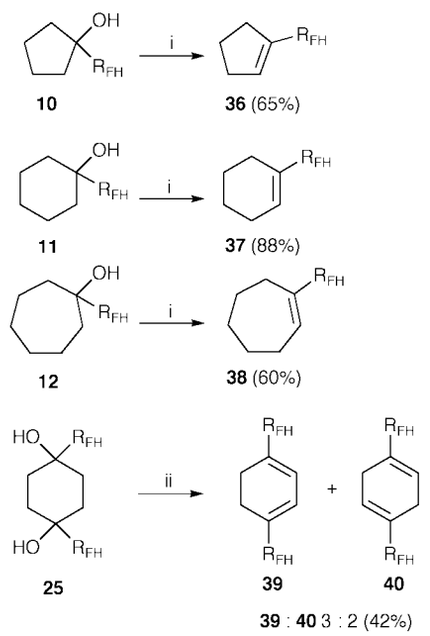
Although the polyfluoroalkyl group is, of course, strongly electron withdrawing, the hydroxy groups in the polyfluoroalkyl adducts remain sufficiently nucleophilic for esterification to occur. Reaction of **10** with acetyl, benzoyl and methacroyl chloride gave the esters **31**, **32** and **33** respectively (Scheme 2), although **33** polymerised slowly on standing at room temperature. Diol **27** provides the diester **34** upon acetylation (Scheme 2), demonstrating that such polyfluoroalkyl-diols could be used for the synthesis of various fluorinated polyesters. Silylation of **10** with trimethylsilyl chloride at rt in the presence of pyridine gave silyl ether **35** (Scheme 2).

Dehydration of alcohol adducts **10**, **11** and **12** using thionyl chloride (or a mixture of thionyl chloride and pyridine) gave the corresponding alkene derivatives **36**, **37** and **38** respectively (Scheme 3) and in a similar process, diol **25** gave a mixture of dienes **39** and **40**, in a 60 : 40 ratio (Scheme 3). The mechanism of dehydration is most likely that shown in Scheme 4, where reaction of the alcohol with thionyl chloride will lead to nucleophilic displacement of chloride ion which can, subsequently, act as a base to promote the elimination process.

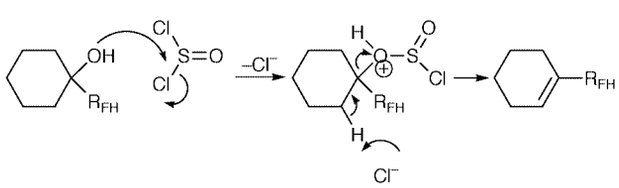
Whilst the chemistry of perfluorinated alkenes is well established, alkenes with both alkyl and perfluoroalkyl substituents are less common and few reports concerning their reactivity have been documented. For example, Henne[20] reported that 3,3,3-trifluoropropene reacts with a mixture of hydrogen



Scheme 2 $R_{FH} = -CF_2CFHCF_3$.



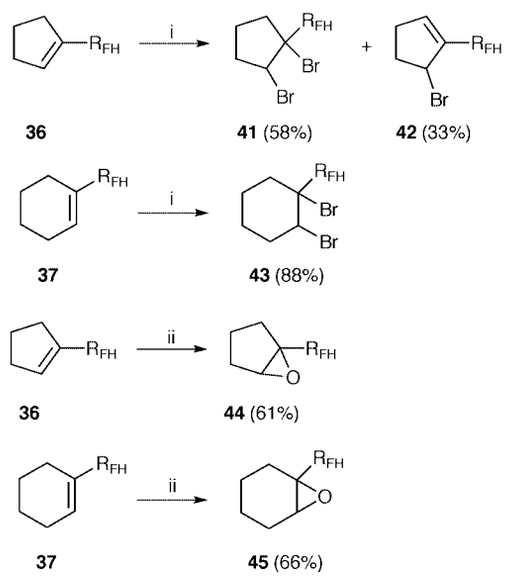
Scheme 3 *Reagents and conditions*: (i) $SOCl_2$, reflux, 24 h; (ii) $SOCl_2$, pyridine, 0 °C. $R_{FH} = -CF_2CFHCF_3$.



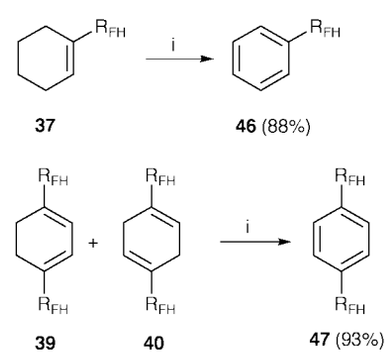
Scheme 4 $R_{FH} = -CF_2CFHCF_3$.

chloride and aluminium trichloride to give the terminal chloroalkane derivative and Myhre[21] described dimerisation of the same alkene in fluorosulfonic acid. In probing electrophilic attack on systems **36** and **37** (Scheme 5), we found that bromination and epoxidation, using bromine and *m*-chloroperbenzoic acid respectively, occurs albeit relatively slowly. Bromination of **36** gave **42** as a by-product, formed upon dehydrobromination of dibromide **41**.

Dehydrogenation of cyclohexene and cyclohexadiene derivatives **37** and **39**, **40** by sulfur, *via* a free radical process, affords polyfluoroalkylated aromatic systems **46** and **47** respectively, in excellent yield (Scheme 6).



Scheme 5 *Reagents and conditions*: i, Br_2, CH_2Cl_2, rt, 12 h; ii, *m*-chloroperbenzoic acid, CH_2Cl_2, reflux, 7 d. $R_{FH} = -CF_2CFHCF_3$.



Scheme 6 *Reagents and conditions*: (i) sulfur, 225 °C, 24 h. $R_{FH} = -CF_2CFHCF_3$.

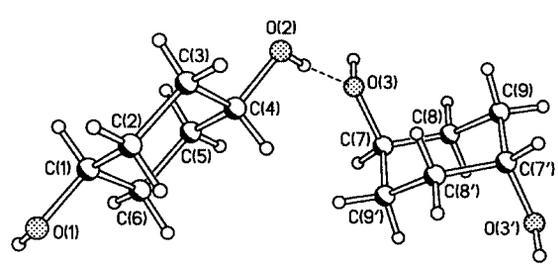


Fig. 5 Two non-equivalent molecules of *trans*-**19** in crystal. Atoms with primed numbers (*n*′) are symmetrically related (to atom *n*) *via* the inversion centre.

In summary, we have further developed an approach involving free-radical chemistry of fluoroalkenes to give high-efficiency routes to new fluorinated alcohols and diols, from which a variety of polyfluoroalkylated alkenes, dienes and aromatic systems can be synthesised. The chemistry of these new fluorine containing 'building blocks' is being pursued.

Crystallography of polyfluoroalkylated derivatives

Structure of *trans*-19. The asymmetric unit (Fig. 5) comprises one molecule (A), which has no crystallographic symmetry but a local molecular symmetry C_i, and a half of another molecule (B), which is situated at a crystallographic inversion centre. In either molecule the cyclohexane ring adopts a chair conformation. However, the hydroxy groups have different orientations: equatorial in A and axial in B, with the average O–C–C–C torsion angles of 178.1 and 66.0°, respectively. All hydroxy

groups are engaged in strong intermolecular hydrogen bonds (O · · · O 2.72–2.75 Å).

R_{FH} derivatives. The crystals of all fluorinated products were of poor quality, due to extreme conformational flexibility (and hence the frequent disorder) of the R_{FH} group. Moreover, reaction of **1** with hexafluoropropene generates a chiral centre ($CF_2C^*HFCF_3$) in the R_{FH} side-chain and for cyclo-1,3-diols, a further stereogenic centre is present at the substituted carbon atom of the ring. There is no evidence that the absolute configurations produced at these two (rather distant) centres, are in any way correlated. Thus, each product comprises a mixture of stereoisomers. Since the steric size of fluorine and hydrogen atoms are not greatly dissimilar, the isomers with opposite configurations of the side chain may form solid solutions (substituting each other), rather than ordered racemic crystals. The coexistence in the crystal of ordered cyclodiol moieties (linked by strong hydrogen bonds) and disordered side-chains, results in the existence of sublattices and in fast drop of diffraction intensity with $\sin\theta/\lambda$, hence poor resolution. All these factors contributed to reduce the precision of the final crystal structures.

Structure of *trans*-23. The asymmetric unit comprises two independent molecules, A and B (Fig. 3). Molecule B does not show any obvious disorder, although large atomic displacement ellipsoids of the terminal CF_3 groups (and of their fluorine atoms especially) indicate extreme flexibility of the side-chains. However, in molecule A both side-chains are disordered in different ways. The fluorine substituent at C(10A) is disordered over two positions, F(9A) and F(9A′), with occupancies of 92(1) and 8(1)%, respectively. In the other chain, the $–CF_2CHF–$ moiety is disordered over two positions with occupancies of 75(2) and 25(2)%; the minor position of the F(3A) atom coincides with the major one of F(1A). In both molecules, the 5-membered ring adopts a half-chair conformation with pseudo-axial orientation hydroxy and pseudo-equatorial R_{FH} chains.

Molecule **23** has four asymmetric carbon atoms: C(1) and C(3) in the ring (which for the *trans* isomer ought to have the same configuration), and C(7) and C(10) in the side-chains. Molecules A and B are *different* diastereomers: for the *R*,*R*-configuration in the ring, the side chains have *S*,*S*-configuration in A and *S*,*R* in B. As the crystal is centrosymmetric, the inversion equivalents of either molecule are also present, with the configurations *S*,*S*,*R*,*R* and *S*,*S*,*R*,*S* respectively.

Two (of the four independent) hydroxy H atoms are engaged in strong intermolecular hydrogen bonds: O(3A)–H · · · O(3B) and O(1B)–H · · · O(3A) ($3/2 - x, y - 1/2, 1/2 - z$) with O · · · O distances 2.79(1) and 2.81(1) Å. The other two form relatively short contacts only with fluorine atoms, intermolecular O(1A)–H · · · F(3A) ($1/2 - x$, $y - 1/2$, $1/2 - z$) and intramolecular O(3B)–H · · · F(9B) (O · · · F 2.94 and 2.75 Å). Carbon-bonded fluorine atoms accept hydrogen bonds very reluctantly and usually 'by default' (*i.e.* in the absence of any better acceptors), such bonds being of exceptionally low energy.[22,23]

Structure of *cis*-24. Molecule **24**, like **23**, contains four chiral centres, C(1), C(3), C(8) and C(11). In the *cis*-isomer, the absolute configurations of the former two must be opposite. The asymmetric unit comprises four independent molecules, A, B, C and D (Fig. 4). Six (out of eight) symmetrically independent R_{FH} groups show disorder among the substituents at the asymmetric carbon atom. In molecule A, the F(9) atom is disordered over two positions (occupancy factors $G = 82$ and 18%). In molecule B, atoms F(3), C(9) and F(6) are disordered also over two positions ($G = 73$ and 27%); in molecule C, F(3) ($G = 82$ and 18%) and F(9) ($G = 87$ and 13%); in molecule D, F(3) ($G = 76$ and 24%) and F(9) ($G = 78$ and 22%). In each case, the major and minor components correspond to *opposite*

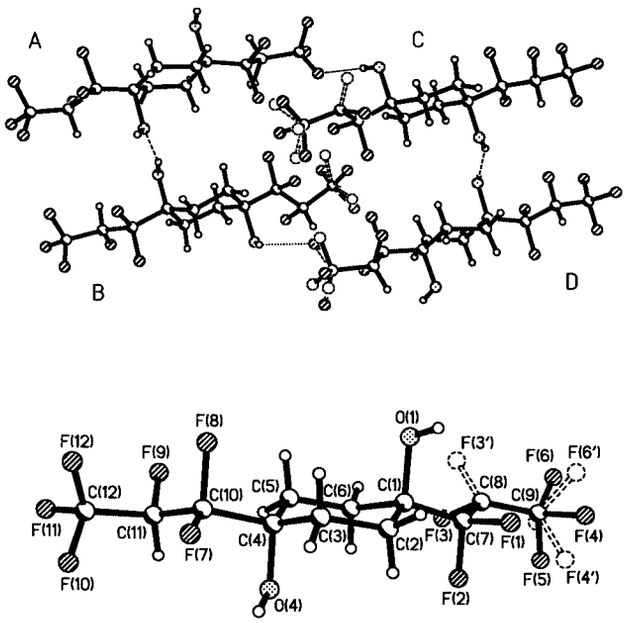


Fig. 6 Top: four independent molecules in the crystal of *trans*-**25**; bottom: molecule A, showing the numbering scheme for each molecule. Minor positions of disordered atoms have primed numbers.

absolute configurations at the chiral centre C(8) or C(11), *i.e.* swapping of the F and H atoms. If the minor components are disregarded, molecules A, B and D comprise the same isomer, with the configurations of the C(1), C(3), C(8) and C(11) atoms being *S*, *R*, *S* and *R*, respectively. Molecule C is an *S*,*R*,*R*,*R*-isomer. The space group is centrosymmetric and therefore the inversion equivalent of each molecule is also present. If the minor components of the disorder are taken into account, then every possible stereoisomer may be present in this crystal.

Nevertheless, the general conformations of all independent molecules are similar, the cyclohexane ring adopting a chair conformation with the axial hydroxy groups and equatorial R_{FH} substituents. In each molecule, one hydroxy H atom participates in an intramolecular and the other in an intermolecular hydrogen bond (O–H · · · O), with the average O · · · O distances of 2.67 Å (intra) and 2.79 Å (inter). The intramolecular bonds link all four independent molecules successively into a helical chain, running in the direction of the crystallographic *z* axis.

Structure of *trans*-25. Molecule **25** has no chirality in the (symmetrically-substituted) ring, the only asymmetric atoms being C(8) and C(11) in the R_{FH} groups. *trans*-**25** crystallises in (a rather uncommon) space group *Pn* with four independent molecules (A, B, C and D) in the asymmetric unit (Fig. 6), which, surprisingly, do not fit any higher crystallographic symmetry. The diffraction pattern shows a strong sublattice (*a*, *b*/2, *c*), due to layered packing of the more ordered ring parts of the molecules. The diffraction was generally weak, even with Cu-Kα radiation.

The conformations of all four molecules are similar. The cyclohexane ring adopts a chair conformation with axial hydroxy groups and equatorial R_{FH} substituents. Practically all fluorine atoms show very large and anisotropic displacement parameters (at 150 K!) indicative of static disorder, especially in CF_3 groups, which also contain high (up to 1.66 e $Å^{-3}$) residual electron density between F atoms. In each of the molecules A, C and D, the disorder of the $C(9)F_3$ group was rationalised as two orientations differing by rotation around the C(8)–C(9) bond. For other fluorine atoms, refinement of multiple positions did not produce meaningful results; probably the disorder is of continuous rather than discrete character. The configurations of the asymmetric atoms C(8) and C(11) are *S*,*S* in molecule B, *R*,*S* in molecule C, *R*,*R* in D. In molecule A, the F(3) atom is evenly disordered between two positions,

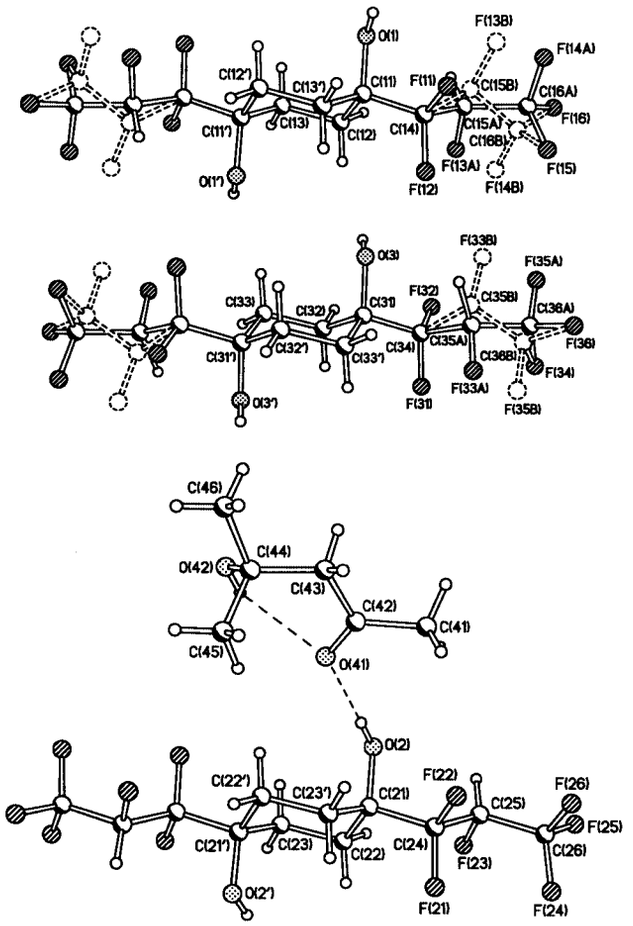


Fig. 7 Molecules of *trans*-**25** and aldol in the crystal of **25**/aldol (showing the disorder). Atoms with primed numbers are symmetrically related *via* the inversion centres.

corresponding to opposite configurations of the C(8) atom, hence this molecular site is occupied by *S*,*S* and *R*,*S* isomers with equal probability. The space group having a symmetry plane, the enantiomers of each configuration are equally present in the crystal, which thus comprises *S*,*S*, *S*,*R* and *R*,*R* isomers in a 5 : 6 : 5 ratio.

Each oxygen atom participates in one intermolecular O · · · O contact of the length (2.78–2.85 Å) characteristic for O–H · · · O hydrogen bonds. These bonds link molecules into two separate infinite chains, parallel to the crystallographic *y* axis: A · · · C · · · A · · · C and B · · · D · · · B · · · D. However, only 4 out of 8 independent hydroxy H atoms can be involved in these bonds. The rest participate in intermolecular O–H · · · F contacts with O · · · F distances of 3.13–3.21 Å and (for idealised hydrogen positions, O–H 0.84 Å) H · · · F distances 2.31–2.48 Å and O–H–F angles 136–175°. Although these contacts can be formally regarded as weak hydrogen bonds,[22,23] they obviously have little effect on the structure, unable even to arrest the disorder of the participating fluorine atoms.

Structure of 25/aldol complex. Crystallisation of *trans*-**25** from acetone unexpectedly yielded crystals of a molecular complex of the latter with aldol. The asymmetric unit comprises three half-molecules of **25**, situated at crystallographically non-equivalent inversion centres, and one aldol molecule in a general position. Thus the overall **25**/aldol ratio is 3 : 2.

In two of the three independent molecules **25,** –CHF–CF_3 groups are disordered in a similar mode (Fig. 7). The C(15), C(16), F(13) and F(14) atoms occupy two sets of positions with occupancies 82.5 and 17.5(7)%; C(35), C(36), F(33) and F(35) also occupy two sets of positions with occupancies 79.6 and 20.4(7)%. In either case, the major and minor positions have opposite absolute configurations of the asymmetric atoms C(15) and C(35). The third molecule **25** is ordered, it (and the major isomers at the other two sites) are *meso*-forms (*S*,*R*).

The aldol molecule has an intramolecular O–H · · · O hydrogen bond, while all hydroxy groups of **25** participate in intermolecular ones. The aldol is an acceptor in two of such intermolecular bonds (and donor in none), thus restoring the balance between the numbers of active hydrogens and possible acceptor sites. Note that **23** and **25**/aldol gave crystals of significantly better quality than **24** and **25**, which may be due to the fact that in the former two all hydroxys participate in strong O–H · · · O bonds, while in **24** and **25** only half of them do and the rest participate in weak O–H · · · F bonds.

Experimental

All solvents were dried before use by literature procedures. NMR spectra were recorded on either a Varian Gemini 200, a Varian VXR 400S or a Bruker AC250 NMR spectrometer with tetramethylsilane and trichlorofluoromethane as internal standards and deuteriochloroform as solvent, unless otherwise stated. In ^{19}F NMR spectra, upfield shifts are quoted as negative. Coupling constants are given in Hz. Mass spectra were recorded on either a VG 7070E spectrometer or a Fisons VG Trio 1000 spectrometer coupled with a Hewlett Packard 5890 series II gas chromatograph. For mixtures of diastereoisomers, the NMR and mass spectral data of the major diastereoisomer obtained are recorded only. Accurate mass measurements were performed by the EPSRC Mass Spectrometry Service, Swansea. IR spectra were recorded on a Perkin-Elmer 1600 FT IR spectrometer using KBr plates while elemental analyses were obtained on either a Perkin-Elmer 240 or a Carlo Erba Elemental Analyser. Melting and boiling points were recorded at atmospheric pressure and are uncorrected. Superscript numbers given as part of boiling point data indicate the pressure (in mmHg) during measurement. Distillations were carried out using a Fischer Spahltrohr MS200 microdistillation apparatus. Gamma ray irradiations were performed in a purpose built shielded chamber fitted with a cobalt-60 source (500 Ce original activity). Column chromatography was performed on silica gel (Merck no. 1-09385) and TLC analysis was performed on silica gel TLC plates (Merck).

General procedure for free radical additions initiated by γ-ray irradiation

A Pyrex Carius tube (*ca.* 60 ml) was charged with the alcohol and acetone (20 ml) and the mixture was degassed three times by freeze–thawing. Hexafluoropropene (HFP) was degassed separately by the same procedure and transferred to the tube, which was cooled in liquid air, at reduced pressure using vacuum line techniques. The tube was sealed under vacuum while frozen and allowed to reach room temperature in a metal sheath. The tube was housed in a purpose built irradiation chamber and irradiated with γ-rays for a period of ten days to give a total dose of *ca.* 10 MRad. The tube was then removed from the chamber, frozen in liquid air and opened. Volatile material was collected *via* vacuum transfer as the tube approached room temperature and the product mixture was collected and purified by either fractional distillation at reduced pressure (Spaltrohr) or column chromatography on silica gel.

Cyclobutanol. Cyclobutanol **3** (5.0 g, 69 mmol), acetone and hexafluoropropene (12.0 g, 80 mmol) gave, after fractional distillation at reduced pressure, *1-(1,1,2,3,3,3-hexafluoropropyl)-cyclobutanol* **9** (12.0 g, 78%) as a colourless liquid; bp^{16} 44–46 °C (Found: C, 37.8; H, 3.5. $C_7H_8F_6O$ requires C, 37.8; H, 3.6%); δ_H 1.8–2.2 (2 H, m, CH_2), 2.5–2.7 (4 H, m, CH_2), 3.14 (1 H, br s, OH), 5.17 (1 H, ddqd, $^2J_{HF}$ 43.2, $^3J_{HF1}$ 18.4, $^3J_{HF}$ 6.0, $^3J_{HF2}$ 3.2, CHF); δ_C 13.10 (s, C-3), 29.85 (s, C-4), 30.21 (s, C-2),

76.13 (dd, $^2J_{CF}$ 31.3, $^2J_{CF}$ 26.4, COH), 83.99 (ddqd, $^1J_{CF}$ 194, $^2J_{CF1}$ 37.7, $^2J_{CF}$ 34.3, $^2J_{CF2}$ 25.5, CFH), 117.43 (ddd, $^1J_{CF1}$ 257, $^1J_{CF2}$ 248, $^2J_{CF}$ 24.0, CF_2), 121.06 (qd, $^1J_{CF}$ 282, $^2J_{CF}$ 25.5, CF_3); δ_F −74.60 (3 F, m, CF_3), −126.47 and −128.41 (2 F, AB, J_{AB} 275, CF_2), −213.30 (1 F, dm, $^2J_{HF}$ 43.2, CFH); *m/z* (EI^+) 194 (100), 174 (15), 93 (64), 71 (39), 69 (33), 43 (64).

Cyclopentanol. Cyclopentanol **4** (4.8 g, 56 mmol), acetone and hexafluoropropene (9.6 g, 64 mmol) gave, after fractional distillation at reduced pressure, *1-(1,1,2,3,3,3-hexafluoropropyl)cyclopentanol* **10** (9.5 g, 72%) as a colourless liquid; bp[4] 37–38 °C (Found: C, 40.7; H, 4.3. $C_8H_{10}F_6O$ requires C, 40.7; H, 4.2%); δ_H 1.65–2.20 (8 H, m, CH_2), 5.26 (1 H, ddq, $^2J_{HF}$ 43.2, $^3J_{HF}$ 19.2, $^3J_{HF}$ 6.4, CHF); δ_C 23.09 (s, C-4), 24.24 (d, $^4J_{CF}$ 1.9, C-3), 34.10 (dd, $^3J_{CF}$ 5.3, $^3J_{CF}$ 4.2, C-2), 35.21 (m, C-5), 83.33 (m, CFH), 83.61 (dd, $^2J_{CF}$ 27.1, $^2J_{CF}$ 23.6, COH), 118.38 (ddd, $^1J_{CF1}$ 262, $^1J_{CF2}$ 247, $^2J_{CF}$ 23.6, CF_2), 121.16 (qd, $^1J_{CF}$ 283, $^2J_{CF}$ 26.0, CF_3); δ_F −74.22 (3 F, m, CF_3), −120.97 and −126.77 (2 F, AB, J_{AB} 275, CF_2), −209.65 (1 F, dm, $^2J_{FH}$ 43.2, CFH); *m/z* (EI^+) 199 (27%), 85 (100), 69 (59), 67 (79), 41 (93).

Cyclohexanol. Cyclohexanol **5** (12.5 g, 125 mmol), acetone and hexafluoropropene (22.0 g, 147 mmol) gave, after fractional distillation at reduced pressure, *1-(1,1,2,3,3,3-hexafluoropropyl)cyclohexanol* **11** (23.8 g, 76%) as colourless crystals; mp 42–43 °C; bp[9] 59–60 °C (Found: C, 43.3; H, 4.8. $C_9H_{12}F_6O$ requires C, 43.3; H, 4.8%); $\delta_H(CD_3COCD_3)$ 1.16–1.90 (10 H, m, CH_2), 5.68 (1 H, ddqd, $^2J_{HF}$ 42.8, $^3J_{HF1}$ 17.2, $^3J_{HF}$ 6.8, $^3J_{HF2}$ 1.6, CFH); $\delta_C(CD_3COCD_3)$ 21.07 (s, C-3), 21.22 (s, C-5), 25.88 (s, C-4), 29.06 (t, $^3J_{CF}$ 4.6, C-2), 30.41 (m, C-6), 73.84 (t, $^2J_{CF}$ 24.3, COH), 83.56 (ddqd, $^1J_{CF}$ 193, $^2J_{CF1}$ 37.0, $^2J_{CF}$ 33.6, $^2J_{CF2}$ 23.6, CFH), 119.49 (ddd, $^1J_{CF1}$ 264, $^1J_{CF2}$ 251, $^2J_{CF}$ 21.0, CF_2), 122.55 (qd, $^1J_{CF}$ 282, $^2J_{CF}$ 26.4, CF_3); $\delta_F(CD_3COCD_3)$ −74.77 (3 F, m, CF_3), −126.91 and −128.51 (2 F, AB, J_{AB} 272, CF_2), −208.27 (1 F, dm, $^2J_{FH}$ 42.8, CFH); *m/z* (EI^+) 233 (18%, $M^+ - OH$), 213 (24), 151 (7), 99 (97, $M^+ - CF_2CFHCF_3$), 81 (100), 69 (51).

Cycloheptanol. Cycloheptanol **6** (13.0 g, 114 mmol), acetone and hexafluoropropene (20.1 g, 134 mmol) gave, after fractional distillation at reduced pressure, *1-(1,1,2,3,3,3-hexafluoropropyl)cycloheptanol* **12** (20.5 g, 68%) as a colourless liquid; bp[5] 64–67 °C (Found: C, 45.4; H, 5.3. $C_{10}H_{14}F_6O$ requires C, 45.5; H, 5.3%); δ_H 1.48–2.16 (13 H, m, CH_2 and OH), 5.20 (1 H, ddqd, $^2J_{HF}$ 44.0, $^3J_{HF1}$ 17.6, $^3J_{HF}$ 6.8, $^3J_{HF2}$ 1.2, CFH); δ_C 21.59 (s, C-4), 21.87 (s, C-5), 29.55 (s, C-3), 29.74 (s, C-6), 33.91 (dd, $^3J_{CF}$ 2.6, $^3J_{CF}$ 2.3, C-2), 34.10 (d, $^3J_{CF}$ 4.6, C-7), 77.53 (t, $^2J_{CF}$ 24.0, COH), 83.05 (ddqd, $^1J_{CF}$ 196, $^2J_{CF1}$ 37.7, $^2J_{CF}$ 33.5, $^2J_{CF2}$ 23.6, CFH), 118.71 (ddd, $^1J_{CF1}$ 266, $^1J_{CF2}$ 251, $^2J_{CF}$ 20.5, CF_2), 121.17 (qd, $^1J_{CF}$ 283, $^2J_{CF}$ 26.4, CF_3); δ_F −74.22 (3 F, m, CF_3), −122.45 and −127.25 (2 F, AB, J_{AB} 278, CF_2), −206.71 (1 F, dm, $^2J_{FH}$ 44.0, CFH); *m/z* (EI^+) 207 (3%), 151 (3), 113 (100), 95 (63), 69 (35), 55 (52), 41 (48).

Cyclooctanol. Cyclooctanol **7** (14.2 g, 111 mmol), acetone and hexafluoropropene (19.2 g, 128 mmol) gave *1-(1,1,2,3,3,3-hexafluoropropyl)cyclooctanol* **13** (5.6 g, 18%); bp 198–200 °C (Found: *m/z* $[M - R_{FH}]^+$, 127.1123. $C_{11}H_{16}F_6O$ requires *m/z* $[M - R_{FH}]^+$, 127.1123); δ_H 1.40–1.97 (14 H, m, CH_2), 5.24 (1 H, ddq, $^2J_{HF}$ 43.6, $^3J_{HF1}$ 18.0, $^3J_{HF}$ 6.4, CFH); δ_C 21.30, 21.39, 24.99, 27.09 and 27.34 (all s, all CH_2), 29.68 (t, $^3J_{CF}$ 3.0, C-2), 30.02 (d, $^3J_{CF}$ 4.9, C-8), 77.54 (m, COH), 82.78 (ddqd, $^1J_{CF}$ 196, $^2J_{CF1}$ 37.0, $^2J_{CF}$ 34.0, $^2J_{CF2}$ 23.6, CFH), 118.89 (ddd, $^1J_{CF1}$ 267, $^1J_{CF2}$ 252, $^2J_{CF}$ 21.4, CF_2), 121.16 (qd, $^1J_{CF}$ 283, $^2J_{CF}$ 26.4, CF_3); δ_F −73.97 (3 F, m, CF_3), −121.77 and −124.49 (2 F, AB, J_{AB} 278, CF_2), −206.78 (1 F, dm, $^2J_{FH}$ 43.6, CFH); *m/z* (EI^+) 127 (83%), 69 (46), 67 (57), 55 (66), 41 (100); and a mixture of di-adducts **15** (19.0 g, 40%) which were not separated but whose mass spectral data were consistent with *1,x-bis-(1,1,2,3,3,3-hexafluoropropyl)cyclooctanol*; *m/z* (EI^+) 277 (44%), 151 (18), 69 (76), 55 (78), 43 (88), 41 (100).

***exo*-Bicyclo[2.2.1]heptan-2-ol.** *exo*-Bicyclo[2.2.1]heptan-2-ol **8** (2.7 g, 24 mmol), acetone and hexafluoropropene (4.2 g, 28 mmol) gave, after purification by column chromatography over silica gel, *2-(1,1,2,3,3,3-hexafluoropropyl)bicyclo[2.2.1]heptan-2-ol* **14** (3.4 g, 54%) as a colourless liquid and as a mixture of diastereoisomers; bp 184–186 °C (Found: *m/z* $[M]^+$, 262.0781. $C_{10}H_{12}F_6O$ requires *m/z* $[M]^+$, 262.0792); δ_H 1.09–2.64 (10 H, m, CH and CH_2), 5.27 (1 H, ddqd, $^2J_{HF}$ 43.2, $^3J_{HF1}$ 17.6, $^3J_{HF}$ 6.4, $^3J_{HF2}$ 2.0, CFH); δ_C 22.48 (s, C-5), 27.61 (s, C-6), 35.90 (s, C-4), 38.96 (d, $^4J_{CF}$ 5.7, C-7), 42.23 (m, C-1 and C-3), 80.72 (t, $^2J_{CF}$ 25.5, COH), 83.60 (ddqd, $^1J_{CF}$ 195, $^2J_{CF1}$ 37.7, $^2J_{CF}$ 33.9, $^2J_{CF2}$ 24.8, CFH), 118.70 (ddd, $^1J_{CF1}$ 263, $^1J_{CF2}$ 249, $^2J_{CF}$ 22.1, CF_2), 121.21 (qd, $^1J_{CF}$ 282, $^2J_{CF}$ 25.9, CF_3); δ_F −74.18 (3 F, m, CF_3), −119.63 and −122.29 (2 F, AB, J_{AB} 282, CF_2), −207.90 (1 F, dm, $^2J_{FH}$ 43.2, CFH); *m/z* (EI^+) 244 (11%), 111 (44), 93 (22), 68 (100), 67 (82).

Cyclopentane-1,3-diol. Cyclopentane-1,3-diol **16** (5.0 g, 49 mmol), acetone and hexafluoropropene (17.4 g, 231 mmol) gave, after fractional distillation followed by column chromatography over silica gel, *1,3-bis(1,1,2,3,3,3-hexafluoropropyl)-cyclopentane-1,3-diol* **23** (12.2 g, 63%) as a colourless liquid and as a mixture of diastereoisomers; bp[4] 65–67 °C (colourless crystals after distillation) (Found: C, 32.9; H, 2.4. $C_{11}H_{10}F_{12}O_2$ requires C, 32.8; H, 2.5%); $\delta_H(CD_3COCD_3)$ 2.05–2.65 (3 H, m, CH_2), 5.13–5.31 (1 H, m, OH), 5.68 (1 H, ddq, $^2J_{HF}$ 42.8, $^3J_{HF1}$ 19.2, $^3J_{HF}$ 6.0, CFH); $\delta_C(CD_3COCD_3)$ 33.31 (d, $^3J_{CF}$ 3.4, C-5), 34.32 (s, C-4), 43.04 (d, $^3J_{CF}$ 4.2, C-2), 82.08–84.08 (m, COH), 84.72–85.67 (m, CFH), 119.43 (tm, $^1J_{CF}$ 254, CF_2), 122.61 (qd, $^1J_{CF}$ 282, $^2J_{CF}$ 25.5, CF_3); $\delta_F(CD_3COCD_3)$ −73.87 (3 F, s, CF_3), −122.04 and −126.04 (2 F, AB, J_{AB} 274, CF_2), −209.94 (1 F, br d, $^2J_{FH}$ 42.9, CFH); *m/z* (EI^+) 325 (9%), 251 (74), 233 (100), 205 (15), 185 (11), 159 (14), 151 (28), 145 (18), 69 (66), 43 (56).

Cyclohexane-1,2-diol. Cyclohexane-1,2-diol **17** (6.5 g, 60 mmol), acetone and hexafluoropropene (20.0 g, 135 mmol) were recovered unchanged after irradiation.

Cyclohexane-1,3-diol. Cyclohexane-1,3-diol **18** (2.5 g, 22 mmol), acetone and hexafluoropropene (7.5 g, 50 mmol) gave, after column chromatography on silica gel, *1,3-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane-1,3-diol* **24** (4.1 g, 45%) as a white solid and as a mixture of diastereoisomers; mp 84–86 °C (Found: C, 34.9; H, 2.8. $C_{12}H_{12}F_{12}O_2$ requires C, 34.6; H, 2.9%); $\delta_H(CD_3COCD_3)$ 1.61–2.18 (8 H, m, CH_2), 5.11–5.35 (2 H, m, CFH); $\delta_C(CD_3COCD_3)$ 14.81 (s, C-5), 28.03 (m, C-6), 29.31 (m, C-4), 29.60 (m, C-2), 75.27 (m, C-1 and C-3), 82.70 (dm, $^1J_{CF}$ 196, CFH), 116.85 (m, CF_2), 121.01 (qm, $^1J_{CF}$ 248, CF_3); $\delta_F(CD_3COCD_3)$ −73.95 (3 F, m, CF_3), −126.50 (2 F, m, CF_2), −208.07 (1 F, m, CFH); *m/z* (EI^+) 339 (4%), 265 (53), 247 (100), 219 (20), 199 (22), 159 (35), 151 (15), 69 (28); and *1-(1,1,2,3,3,3-hexafluoropropyl)cyclohexane-1,3-diol* **29** (1.8 g, 30%) as white crystals and as a mixture of diastereoisomers; mp 58–59 °C (Found: C, 40.5; H, 4.5. $C_9H_{12}F_6O_2$ requires C, 40.6; H, 4.5%); $\delta_H(CD_3COCD_3)$ 1.69 (8 H, m, CH_2), 2.93 (2 H, s, OH), 3.88 (1 H, m, CH), 5.71 (1 H, m, CFH); $\delta_C(CD_3COCD_3)$ 19.55 (s, C-5), 28.52 (s, C-4), 35.75 (s, C-6), 38.40 (t, $^3J_{CF}$ 4.2, C-2), 66.23 (s, C-3), 75.91 (m, C-1), 83.40 (dm, $^1J_{CF}$ 180, CFH), 119.1 (dm, $^1J_{CF}$ 249, CF_2), 122.5 (qd, $^1J_{CF}$ 283, $^2J_{CF}$ 26.4, CF_3); $\delta_F(CD_3COCD_3)$ −74.72 (3 F, m, CF_3), −126.53 and −128.26 (2 F, AB, J_{AB} 271, CF_2), −208.4 (2 F, m, CFH); *m/z* (EI^+) 247 (1%, $M^+ - OH$), 115 (26), 69 (29).

Cyclohexane-1,4-diol. Cyclohexane-1,4-diol **19** (2.5 g, 22 mmol), acetone and hexafluoropropene (7.5 g, 50 mmol) gave, after column chromatography on silica gel, *1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane-1,4-diol* **25** (7.6 g, 83%) as colourless crystals and as a mixture of diastereoisomers; mp 105–107 °C (Found: C, 34.8; H, 2.9. $C_{12}H_{12}F_{12}O_2$ requires C, 34.6; H, 2.9%); $\delta_H(CD_3COCD_3)$ 1.5–2.1 (8 H, m, CH_2), 5.25 (2 H, dm,

$^2J_{HF}$ 36.0, CFH); $\delta_C(CD_3COCD_3)$ 23.96 (m, C-2 and C-3), 73.19 (t, $^2J_{CF}$ 23.6, COH), 83.61 (dm, $^1J_{CF}$ 193, CFH), 118.00 (ddd, $^1J_{CF}$ 264, $^1J_{CF}$ 250, $^2J_{CF}$ 26.0, CF_2), 121.30 (qd, $^1J_{CF}$ 283, $^2J_{CF}$ 26.4, CF_3); $\delta_F(CD_3COCD_3)$ −74.33 (3 F, m, CF_3), −126.44 and −128.38 (2 F, AB, J_{AB} 271, CF_2), −207.66 (1 F, dm, $^2J_{FH}$ 36.0, CFH); *m/z* (EI^+) 265 ($M^+ - CF_2CFHCF_3$, 47%), 247 (100), 151 (8), 69 (17).

Propane-1,3-diol. Propane-1,3-diol **20** (3.6 g, 60 mmol), acetone and hexafluoropropene (20.7 g, 138 mmol) gave, after column chromatography over silica gel (1:2, dichloromethane:ethyl acetate), *1,1,1,2,3,3,7,7,8,9,9,9-dodecafluorononane-4,6-diol* **26** (9.6 g, 42%) as a colourless liquid and as a mixture of diastereoisomers; δ_H 2.02 (2 H, s, CH_2), 4.31 (1 H, m, CH), 5.13 (2 H, dm, $^2J_{HF}$ 46.4, CFH); δ_C 27.83 (m, CH_2), 67.67 (m, COH), 83.74 (dm, $^1J_{CF}$ 196, CFH), 117.62 (m, CF_2), 120.72 (qm, $^1J_{CF}$ 291, CF_3); δ_F −74.61 (3 F, m, CF_3), −120.65 and −125.51 (2 F, AB, J_{AB} 275, CF_2), −214.50 (1 F, m, CFH); *m/z* (EI^+) 225 (13%), 159 (19), 113 (11), 77 (71), 69 (90), 45 (100).

Pentane-2,4-diol. Pentane-2,4-diol **21** (7.3 g, 70 mmol), acetone and hexafluoropropene (24.7 g, 165 mmol) gave, after column chromatography over silica gel (5:1, dichloromethane:hexane), *1,1,1,2,3,3,7,7,8,9,9,9-dodecafluoro-4,6-dimethylnonane-4,6-diol* **27** (21.2 g, 75%) as white needles and as a mixture of diastereoisomers; mp 87–88 °C (Found: C, 32.9; H, 3.0. $C_{11}H_{12}F_{12}O_2$ requires C, 32.7; H, 3.0%); δ_H 1.52–1.65 (6 H, m, CH_3), 2.03–2.17 (2 H, m, CH_2), 5.25 (2 H, dm, $^2J_{HF}$ 43.6, CFH); $\delta_C(CD_3COCD_3)$ 20.25 (s, CH_3), 35.41 (s, CH_2), 75.63 (t, $^2J_{CF}$ 22.9, COH), 83.46 (dddq, $^1J_{CF}$ 193, $^2J_{CF1}$ 36.6, $^2J_{CF2}$ 33.2, $^2J_{CF}$ 23.3, CFH), 119.44 (ddd, $^1J_{CF1}$ 267, $^1J_{CF2}$ 253, $^2J_{CF}$ 20.2, CF_2), 122.48 (qd, $^1J_{CF}$ 282, $^2J_{CF}$ 26.3, CF_3); δ_F −73.92 (3 F, s, CF_3), −73.93 (3 F, s, CF_3), −120.92 and −126.12 (2 F, AB, J_{AB} 274, CF_2), −206.40 (2 F, br m, CFH); *m/z* (EI^+) 253 (8%), 195 (12), 155 (12), 151 (7), 91 (17), 69 (26), 43 (100).

Hexane-2,5-diol. Hexane-2,5-diol **22** (7.9 g, 67 mmol), acetone and hexafluoropropene (23.5 g, 157 mmol) gave, after fractional distillation at reduced pressure, *1,1,1,2,3,3,8,8,9,10,10,10-dodecafluoro-4,7-dimethyldecane-4,7-diol* **28** (9.5 g, 34%) as a colourless liquid and as a mixture of diastereoisomers; bp[3] 63–66 °C (Found: M^-, 417.070250. $C_{12}H_{13}F_{12}O_2$ requires M^-, 417.072394); δ_H 1.30–1.42 (6 H, m, CH_3), 1.75–1.96 (4 H, m, CH_2), 5.23 (2 H, dm, $^2J_{HF}$ 43.6, CHF); δ_C 19.51 (s, CH_3), 28.17 (s, CH_2), 74.50 (m, COH), 83.07 (dm, $^1J_{CF}$ 196, CFH), 118.36 (m, CF_2), 120.96 (qd, $^1J_{CF}$ 283, $^2J_{CF}$ 26.4, CF_3); δ_F −74.01 (3 F, s, CF_3), −121.29 to −127.05 (2 F, m, CF_2), −206.98 (1 F, m, CFH); *m/z* (EI^+) 267 (7%), 249 (4), 229 (5), 195 (11), 155 (7), 151 (3), 105 (8), 69 (5), 55 (13), 43 (100).

General procedure for free radical reactions initiated by di-*tert*-butyl peroxide

An autoclave (*ca.* 500 ml), fitted with a bursting disc (maximum working pressure approx. 200 bar) was charged with the alcohol and di-*tert*-butyl peroxide, evacuated and sealed. The resulting mixture and the fluoroalkene were degassed separately by freeze–thawing and transferred to the autoclave at reduced pressure using vacuum line techniques. The autoclave was closed while frozen, transferred to a purpose built chamber and heated at 140 °C for 24 hours in a thermostatically controlled rocking furnace. The autoclave was frozen in liquid air and volatile material was collected by vacuum transfer as the autoclave approached room temperature. The autoclave was opened and the product mixture was collected and purified by either column chromatography on silica gel or distillation under reduced pressure.

Cyclopentanol. A mixture of cyclopentanol **4** (65.0 g, 760 mmol), hexafluoropropene (120.0 g, 800 mmol) and di-*tert*-butyl peroxide (5.9 g, 40 mmol) gave *1-(1,1,2,3,3,3-hexafluoropropyl)cyclopentanol* **10** (117.2 g, 65%); spectral data as above.

Cyclohexanol. A mixture of cyclohexanol **5** (75.0 g, 750 mmol), hexafluoropropene (120.1 g, 805 mmol) and di-*tert*-butyl peroxide (5.9 g, 40 mmol) gave *1-(1,1,2,3,3,3-hexafluoropropyl)cyclohexanol* **11** (122.5 g, 65%); spectral data as above.

Reactions of polyfluoroalkyl alcohol adducts. Esterification—general procedure

A mixture consisting of the alcohol and an excess of the acid chloride was heated at reflux temperature for 24 hours. The cooled reaction mixture was added to water and extracted with dichloromethane (3 × 20 ml). The organic extracts were dried ($MgSO_4$) and evaporated to give a crude product which was purified by column chromatography on silica gel using dichloromethane as eluant.

1-(1,1,2,3,3,3-Hexafluoropropyl)cyclopentyl acetate 31. 1-(1,1,2,3,3,3-Hexafluoropropyl)cyclopentanol **10** (4.5 g, 19 mmol) and acetyl chloride (20 ml) gave *1-(1,1,2,3,3,3-hexafluoropropyl)cyclopentyl acetate* **31** (4.1 g, 78%) as a colourless liquid; bp 166–168 °C (Found: C, 43.1; H, 4.3. $C_{10}H_{12}F_6O_2$ requires C, 43.2; H, 4.3%); ν_{max}/cm^{-1} 1752 (C=O); δ_H 1.65–2.2 (11 H, m, CH_2 and CH_3), 5.15 (1 H, ddqd, $^2J_{HF}$ 42.6, $^3J_{HF1}$ 18.8, $^3J_{HF}$ 6.0, $^3J_{HF2}$ 2.0, CFH); δ_C 21.85 (s, CH_3), 25.40 (s, C-3), 26.14 (s, C-3), 32.49 (s, C-2), 32.64 (s, C-2), 84.40 (ddqd, $^1J_{CF}$ 197, $^2J_{CF1}$ 40.0, $^2J_{CF}$ 34.3, $^2J_{CF2}$ 24.8, CFH), 91.83 (dd, $^2J_{CF1}$ 30.9, $^2J_{CF2}$ 23.2, C-1), 117.51 (ddd, $^1J_{CF1}$ 258, $^1J_{CF2}$ 252, $^2J_{CF}$ 22.5, CF_2), 120.93 (qd, $^1J_{CF}$ 282, $^2J_{CF}$ 25.9, CF_3), 168.45 (s, C=O); δ_F −74.29 (3 F, m, CF_3), −116.57 and −125.88 (2 F, AB, J_{AB} 277, CF_2), −208.76 (1 F, dm, $^2J_{HF}$ 42.5, CFH); *m/z* (EI^+) 199 (5%), 85 (12), 69 (21), 43 (100).

1-(1,1,2,3,3,3-Hexafluoropropyl)cyclopentyl benzoate 32. 1-(1,1,2,3,3,3-Hexafluoropropyl)cyclopentanol **10** (3.0 g, 13 mmol) and benzoyl chloride (20 ml) at 70 °C gave *1-(1,1,2,3,3,3-hexafluoropropyl)cyclopentyl benzoate* **32** (3.1 g, 72%) as a colourless liquid; bp 192–194 °C (Found: *m/z* $[M]^+$, 340.0898. $C_{15}H_{14}O_2F_6$ requires *m/z* $[M]^+$ 340.0898); ν_{max}/cm^{-1} 1775 (C=O); δ_H 1.7–2.2 (4 H, m, 3-CH_2), 2.3–2.4 (4 H, m, 2-CH_2), 5.32 (1 H, ddqd, $^2J_{HF}$ 43.6, $^3J_{HF1}$ 18.8, $^3J_{HF}$ 6.0, $^3J_{HF2}$ 2.0, CFH), 7.59 (1 H, t, $^3J_{HH}$ 7.2, *p*-Ar-H), 7.68 (2 H, t, $^3J_{HH}$ 7.2, *m*-Ar-H), 8.11 (2 H, m, *o*-Ar-H); δ_C 25.45 and 26.08 (both s, both 3-CH_2), 32.56 and 32.74 (both s, both 2-CH_2), 84.43 (ddqd, $^1J_{CF}$ 198, $^2J_{CF1}$ 39.7, $^2J_{CF}$ 33.9, $^2J_{CF2}$ 24.3, CFH), 92.36 (dd, $^2J_{CF1}$ 30.9, $^2J_{CF2}$ 24.4, C-O), 117.51 (ddd, $^1J_{CF1}$ 260, $^1J_{CF2}$ 252, $^2J_{CF}$ 22.4, CF_2), 120.93 (qd, $^1J_{CF}$ 283, $^2J_{CF}$ 25.8, CF_3), 128.55 (s, Ar-C3), 129.43 (s, Ar-C2), 130.14 (s, Ar-C1), 133.39 (s, Ar-C4), 168.45 (s, C=O); δ_F −73.99 (3 F, m, CF_3), −116.55 and −124.81 (2 F, AB, J_{AB} 278, CF_2), −207.57 (1 F, dm, $^2J_{HF}$ 43.6, CFH); *m/z* (EI^+) 99 (100%), 81 (86), 79 (14), 69 (20).

1-(1,1,2,3,3,3-Hexafluoropropyl)cyclopentyl methacrylate 33. 1-(1,1,2,3,3,3-Hexafluoropropyl)cyclopentanol **10** (2.4 g, 10 mmol) and methacroyl chloride (20 ml) at 70 °C for 96 h gave *1-(1,1,2,3,3,3-hexafluoropropyl)cyclopentyl methacrylate* **33** (1.6 g, 52%) as a colourless liquid which polymerised upon standing; δ_H 1.6–2.9 (8 H, m, CH_2), 1.85 (3 H, s, CH_3), 5.16 (1 H, ddqd, $^2J_{HF}$ 43.6, $^3J_{HF1}$ 18.8, $^3J_{HF}$ 6.4, $^3J_{HF2}$ 2.4, CFH), 5.54 (1 H, m, =C–H), 5.96 (1 H, m, =C–H); δ_C 18.22 (s, CH_3), 25.48 (s, C-3), 26.19 (s, C-3), 32.52 (m, C-2), 84.44 (m, CFH), 92.00 (dd, $^2J_{CF1}$ 30.5, $^2J_{CF2}$ 24.8, C-O), 117.51 (ddd, $^1J_{CF1}$ 259, $^1J_{CF2}$ 253, $^2J_{CF}$ 23.6, CF_2), 120.88 (qd, $^1J_{CF}$ 283, $^2J_{CF}$ 25.5, CF_3), 126.39 (s, $=CH_2$), 136.47 (s, –C=), 164.87 (s, C=O); δ_F −74.11 (3 F, m, CF_3), −116.54 and −125.34 (2 F, AB, J_{AB} 277, CF_2), −207.96 (1 F, dm, $^2J_{HF}$ 43.6, CFH); *m/z* (EI^+) 198 (33%), 97 (12), 87 (99), 69 (100).

1,1,1,2,3,3,7,7,8,9,9,9-Dodecafluoro-4,6-dimethylnonane-4,6-diyl diacetate 34. 1,1,1,2,3,3,7,7,8,9,9,9-Dodecafluoro-4,6-dimethylnonane-4,6-diol **27** (1.5 g, 4 mmol) and acetyl chloride (20 ml) gave *1,1,1,2,3,3,7,7,8,9,9,9-dodecafluoro-4,6-dimethylnonane-4,6-diyl diacetate* **34** (1.3 g, 72%) as a colourless liquid and as a mixture of diastereoisomers; bp 235–239 °C (Found: C, 36.7; H, 3.3. $C_{15}H_{16}F_{12}O_4$ requires C, 36.9; H, 3.3%); ν_{max}/cm^{-1} 1760 (C=O); δ_H 1.82 (3 H, m, CH_3), 2.02 (3 H, s, CH_3–C=O), 2.81 (1 H, s, CH_2), 5.23 (1 H, m, CFH); δ_C 19.73 (m, CH_3), 21.80 (s, *C*H_3–C=O), 35.77 (m, CH_2), 83.90 (m, CFH), 83.22 (m, C–OH), 116.7 (m, CF_2), 120.78 (qd, $^1J_{CF}$ 281.4, $^2J_{CF}$ 25.8, CF_3), 169.04 (s, C=O); δ_F −74.16 (3 F, m, CF_3), −117.8 and −122.7 (2 F, AB, J_{AB} 277, CF_2), 207.3 (1 F, m, CFH); *m*/*z* (EI$^+$) 429 (3%), 235 (11), 103 (16), 61 (20), 43 (100).

Silylation

(1-(1,1,2,3,3,3-Hexafluoropropyl)cyclopentyloxy)trimethylsilane 35. 1-(1,1,2,3,3,3-Hexafluoropropyl)cyclopentanol **10** (1.0 g, 4 mmol) was added to a mixture of trimethylsilyl chloride (0.9 g, 8 mmol) and pyridine (10 ml) at 0 °C, and the resulting solution was stirred at rt for 2 h. The cooled reaction mixture was added to water and extracted with dichloromethane. The organic extracts were dried ($MgSO_4$) and evaporated to give a crude product. Purification by column chromatography on silica gel using dichloromethane–hexane (8:1) as eluant gave *(1-(1,1,2,3,3,3-hexafluoropropyl)cyclopentyloxy)trimethylsilane* **35** (1.0 g, 84%) as a colourless liquid; bp 154–155 °C (Found: *m*/*z* [M − H]$^+$, 307.0954. $C_{11}H_{18}OSiF_6$ requires *m*/*z* [M − H]$^+$, 307.0953); δ_H 0.17 (9 H, s, CH_3), 1.6–2.2 (8 H, m, CH_2), 4.10 (1 H, ddqd, $^2J_{HF}$ 43.2, $^3J_{HF1}$ 18.4, $^3J_{HF}$ 6.4, $^3J_{HF2}$ 1.2, CFH); δ_C 1.76 (s, CH_3), 23.67 (s, C-3), 24.65 (s, C-3), 33.79 (s, C-2), 36.04 (s, C-2), 82.32 (ddqd, $^1J_{CF}$ 195, $^2J_{CF1}$ 38.9, $^2J_{CF}$ 34.0, $^2J_{CF2}$ 24.0, CFH), 86.26 (dd, $^2J_{CF1}$ 28.6, $^2J_{CF2}$ 22.5, C–O), 118.32 (ddd, $^1J_{CF1}$ 261, $^1J_{CF2}$ 251, $^2J_{CF}$ 23.3, CF_2), 121.33 (qd, $^1J_{CF}$ 283, $^2J_{CF}$ 26.3, CF_3); δ_F −74.59 (3 F, m, CF_3), −120.31 and −127.13 (2 F, AB, J_{AB} 261, CF_2), −209.51 (1 F, dm, $^2J_{HF}$ 43.2, CFH); *m*/*z* (EI$^+$) 199 (13%), 169 (30), 157 (58), 141 (15), 129 (48), 109 (23), 73 (100).

Dehydration—general procedure

A mixture consisting of the alcohol derivative and thionyl chloride was heated at reflux temperature and the gases emitted were passed through an aqueous solution of potassium hydroxide. The cooled mixture was added dropwise to a mixture of ice and dichloromethane. The aqueous solution was extracted three times with dichloromethane and the combined organic extracts were washed twice with water, dried ($MgSO_4$) and concentrated at reduced pressure. Purification by column chromatography on silica gel or fractional distillation gave the alkene.

1-(1,1,2,3,3,3-Hexafluoropropyl)cyclopentene 36. 1-(1,1,2,3,3,3-Hexafluoropropyl)cyclopentanol **10** (18.5 g, 74 mmol) and thionyl chloride (72 ml, 0.88 mol) gave, after fractional distillation, *1-(1,1,2,3,3,3-hexafluoropropyl)cyclopentene* **36** (10.5 g, 65%) as a colourless liquid; bp 128–130 °C (Found: C, 44.0; H, 3.6. $C_8H_8F_6$ requires C, 44.0; H, 3.7%); δ_H 2.00 (2 H, quintet, $^3J_{HH}$ 7.6, H-4), 2.48 (4 H, m, H-2,5), 4.84 (1 H, dddq, $^2J_{HF}$ 44.0, $^3J_{HF1}$ 11.6, $^3J_{HF2}$ 6.0, $^3J_{HF}$ 5.6, CFH), 6.22 (1 H, m, =C–H); δ_C 23.17 (s, C-4), 30.78 (d, $^3J_{CF}$ 1.5, C-5), 32.65 (s, C-3), 86.23 (ddqd, $^1J_{CF}$ 198, $^2J_{CF}$ 36.6, $^2J_{CF}$ 34.0, $^2J_{CF}$ 33.7, CFH), 115.56 (ddd, $^1J_{CF}$ 248, $^1J_{CF}$ 245, $^2J_{CF}$ 22.8, CF_2), 120.63 (qdd, $^1J_{CF}$ 282, $^2J_{CF}$ 26.0, $^3J_{CF}$ 2.6, CF_3), 134.99 (t, $^2J_{CF}$ 24.0, C-1), 135.81 (t, $^3J_{CF}$ 7.2, C-2); δ_F −74.62 (3 F, m, CF_3), −104.50 and −109.46 (2 F, AB, J_{AB} 274, CF_2), −209.97 (1 F, dq, $^2J_{HF}$ 44.0, $^3J_{FF}$ 13.5, CFH); *m*/*z* (EI$^+$) 218 (M$^+$, 7%), 117 (14), 97 (18), 77 (14), 67 (100).

1-(1,1,2,3,3,3-Hexafluoropropyl)cyclohexene 37. 1-(1,1,2,3,3,3-Hexafluoropropyl)cyclohexanol **11** (29.9 g, 120 mmol) and thionyl chloride (104 ml, 1.33 mol) gave, after fractional distillation, *1-(1,1,2,3,3,3-hexafluoropropyl)cyclohexene* **37** (24.4 g, 88%) as a colourless liquid; bp 153–154 °C (Found: C, 46.3; H, 4.3. $C_9H_{10}F_6$ requires C, 46.6; H, 4.3%); δ_H 1.6–1.8 (4 H, m, H-4,5), 2.1–2.2 (4 H, m, H-3,6), 5.60 (1 H, dm, $^2J_{HF}$ 42.4, CFH), 6.30 (1 H, m, =C–H); δ_C 22.03 (s, C-4), 22.47 (s, C-5), 23.44 (s, C-6), 25.29 (s, C-3), 86.15 (ddqd, $^1J_{CF}$ 194, $^2J_{CF1}$ 36.6, $^2J_{CF}$ 33.2, $^2J_{CF2}$ 30.9, CFH), 117.84 (ddd, $^1J_{CF1}$ 249, $^1J_{CF2}$ 246, $^2J_{CF}$ 22.1, CF_2), 122.11 (qdd, $^1J_{CF}$ 282, $^2J_{CF}$ 26.4, $^3J_{CF}$ 3.0, CF_3), 130.26 (t, $^2J_{CF}$ 21.7, C-1), 132.09 (t, $^3J_{CF}$ 9.2, C-2); δ_F −74.90 (3 F, m, CF_3), −110.95 and −113.72 (2 F, AB, J_{AB} 261, CF_2), −212.82 (1 F, dq, $^2J_{HF}$ 42.4, $^3J_{FF}$ 13.9, CFH); *m*/*z* (EI$^+$) 232 (M$^+$, 13%), 131 (17), 103 (14), 81 (100).

1-(1,1,2,3,3,3-Hexafluoropropyl)cycloheptene 38. 1-(1,1,2,3,3,3-Hexafluoropropyl)cycloheptanol **12** (10.4 g, 39 mmol) and thionyl chloride (38 ml, 473 mmol) gave, after column chromatography over silica gel, *1-(1,1,2,3,3,3-hexafluoropropyl)cycloheptene* **38** (5.8 g, 60%) as a colourless liquid; bp 171–174 °C; δ_H 1.4–2.4 (10 H, m, CH_2), 5.58 (1 H, dm, $^2J_{HF}$ 42.4, CFH), 6.46 (1 H, tt, $^3J_{HH}$ 6.4, $^4J_{HF}$ 2.4, =C–H); δ_C 26.44 (s, C-5), 26.97 (s, C-6), 27.57 (s, C-4), 28.58 (s, C-7), 32.70 (s, C-3), 86.10 (dm, $^1J_{CF}$ 194, CFH), 118.42 (ddd, $^1J_{CF1}$ 250, $^1J_{CF2}$ 245, $^2J_{CF}$ 2.4, CF_2), 121.94 (qd, $^1J_{CF}$ 282, $^2J_{CF}$ 25.9, CF_3), 136.02 (t, $^2J_{CF}$ 20.2, C-1), 137.09 (d, $^3J_{CF}$ 8.4, C-2); δ_F −69.52 (3 F, m, CF_3), −105.46 and −108.70 (2 F, AB, J_{AB} 254, CF_2), −206.88 (1 F, m, CFH); *m*/*z* (EI$^+$) 246 (M$^+$, 24%), 103 (20), 95 (100), 77 (17).

1,4-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexa-1,3-hexadiene 39 and 1,4-bis-(1,1,2,3,3,3-hexafluoropropyl)cyclohexa-1,4-diene 40. A mixture containing 1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane-1,4-diol **25** (6.9 g, 17 mmol), thionyl chloride (40.4 g, 340 mmol) and dry pyridine (32.4 g, 410 mmol), gave a mixture of *1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexa-1,3-diene* **39** and *1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexa-1,4-diene* **40** (60:40) (2.7 g, 42%) which could not be separated (Found: M$^+$, 380.0434000. $C_{12}H_8F_{12}$ requires M$^+$, 380.1783600); **39**: δ_H 2.50 (2 H, m, CH_2), 5.7 (2 H, m, CFH), 6.43 (1 H, m, =C–H); δ_F −74.8 (3 F, m, CF_3), −110.75 and −114.45 (2 F, AB, J_{AB} 252, CF_2), −212.7 (1 F, m, CFH); **40**: δ_H 3.08 (2 H, m, CH_2), 5.7 (2 H, m, CFH), 6.62 (1 H, m, =C–H); δ_F −74.8 (3 F, m, CF_3), −110.87 and −114.96 (2 F, AB, J_{AB} 252, CF_2), −212.7 (1 F, m, CFH).

Reactions of alkenes. Bromination—general procedure

A mixture of the alkene derivative and bromine (3.2 g, 20 mmol) was stirred at rt for 12 h. The mixture was diluted with dichloromethane (50 ml) and washed with 10% aqueous sodium metabisulfate. The organic layer was separated and the aqueous layer was further extracted with dichloromethane (2 × 50 ml). The combined organic layers were washed with water, dried ($MgSO_4$) and concentrated under vacuum to yield the dibromo-derivative which was purified by column chromatography on silica gel using dichloromethane as eluant.

1-(1,1,2,3,3,3-Hexafluoropropyl)-1,2-dibromocyclopentane 41. 1-(1,1,2,3,3,3-Hexafluoropropyl)cyclopentene **36** (2.0 g, 9 mmol) and bromine (3.0 g, 19 mmol) gave, after column chromatography, 1-(1,1,2,3,3,3-hexafluoropropyl)-1,2-dibromocyclopentane **41** (2.0 g, 58%) as a colourless liquid and as a mixture of diastereoisomers; bp[5] 63–65 °C (Found: C, 25.5; H, 2.2. $C_8H_8Br_2F_6$ requires C, 25.4; H, 2.1%); δ_H 2.0–2.2 (2 H, m, 4-CH_2), 2.3–2.45 (2 H, m, 3-CH_2), 2.7–3.1 (2 H, m, 4-CH_2), 4.65 (1 H, d, $^3J_{HH}$ 5.2, CHBr), 4.69 (1 H, d, $^3J_{HH}$ 5.2, CHBr), 5.64 (1 H, ddqd, $^2J_{HF}$ 43.2, $^3J_{HF1}$ 18.0, $^3J_{HF}$ 5.6, $^3J_{HF2}$ 2.0, CFH); δ_C 18.43 (s, C-4), 32.98 (d, $^3J_{CF}$ 1.9, C-5), 37.26 (s, C-3), 52.85 (dd, $^3J_{CF1}$ 6.4, $^3J_{CF2}$ 2.7, C-2), 74.84 (t, $^2J_{CF}$ 22.8, C-1), 83.7–88.1 (m, CFH), 116.52 (ddd, $^1J_{CF1}$ 267, $^1J_{CF2}$ 248, $^2J_{CF}$ 26.6, CF_2), 120.71 (qdd, $^1J_{CF}$ 283, $^2J_{CF}$ 25.9, $^3J_{CF}$ 1.5, CF_3); δ_F −73.86 (6 F,

m, CF_3), −100.11 and 112.43 (2 F, AB, J_{AB} 273, CF_2), −209.00 (1 F, m, CFH); *m*/*z* (EI^+) 299 (5%, $M^+ - Br$), 297 (5%, $M^+ - Br$), 217 (100), 197 (14), 177 (12), 127 (24), 67 (42); and, *1-(1,1,2,3,3,3-hexafluoropropyl)-5-bromocyclopentene* **42** (0.9 g, 33%) as a colourless liquid and as a mixture of diastereoisomers (Found: *m*/*z* $[M - Br]^+$, 217.0452. $C_8H_7BrF_6$ requires *m*/*z* $[M - Br]^+$, 217.0452); δ_H 2.8–3.2 (2 H, m, H-4), 5.0–5.4 (4 H, m, H-3,5 and CFH), 6.63 (1 H, m, =C–H); δ_C 45.32 (s, C-4), 45.99 (d, $^3J_{CF}$ 4.6, CBr), 46.99 (s, C-3), 85.08 (dm, $^1J_{CF}$ 197, CFH), 114.63 (ddd, $^1J_{CF1}$ 255, $^1J_{CF2}$ 246, $^2J_{CF}$ 25.9, CF_2), 120.48 (qd, $^1J_{CF}$ 283, $^2J_{CF}$ 25.9, CF_3), 138.42 (t, $^2J_{CF}$ 26.6, C-1), 140.99 (t, $^3J_{CF}$ 7.6, C-2); δ_F −73.38 (3 F, m, CF_3), −107.28 and −109.54 (2 F, AB, J_{AB} 278, CF_2), −208.29 (1 F, dq, $^2J_{HF}$ 43.2, $^3J_{FF}$ 13.2, CFH); *m*/*z* (EI^+) 217 (66%), 197 (15), 127 (22), 115 (100), 95 (22).

1-(1,1,2,3,3,3-Hexafluoropropyl)-1,2-dibromocyclohexane 43. 1-(1,1,2,3,3,3-Hexafluoropropyl)cyclohexene **37** (2.0 g, 9 mmol) and bromine (3.2 g, 20 mmol) gave, after column chromatography, *1-(1,1,2,3,3,3-hexafluoropropyl)-1,2-dibromocyclohexane* **43** (3.0 g, 88%) as a colourless liquid and as a mixture of diastereoisomers; bp[3] 58–60 °C (Found: C, 27.3; H, 2.5. $C_9H_{10}Br_2F_6$ requires C, 27.6; H, 2.6%); δ_H 1.6–2.8 (8 H, m, CH_2), 4.65 (1 H, m, CHBr), 5.72 (1 H, m, CFH); δ_C 19.19 (s, C-4), 21.45 (s, C-5), 26.40 (s, C-6), 32.36 (s, C-3), 48.93 (d, $^3J_{CF}$ 6.0, C-2), 72.71 (t, $^2J_{CF}$ 22.4, C-1), 84.87 (m, CFH), 116.07 (ddd, $^1J_{CF1}$ 269, $^1J_{CF2}$ 251, $^2J_{CF}$ 24.0, CF_2), 120.70 (qd, $^1J_{CF}$ 283, $^2J_{CF}$ 26.4, CF_3); δ_F −73.74 (3 F, m, CF_3), −107.19 and −111.54 (4 F, AB, J_{AB} 274, CF_2), −206.41 (2 F, dm, $^2J_{HF}$ 48, CFH); *m*/*z* (EI^+) 231 (100%), 127 (15), 109 (14).

Epoxidation—general procedure

m-Chloroperbenzoic acid (4.8 g, 28 mmol) was added to the alkene derivative and dichloromethane (20 ml) over a period of 30 minutes and the mixture was heated at reflux temperature for 7 d. The solution was cooled to rt and excess dry KF was added. The resulting mixture was stirred at rt for 1 h and the solids were removed by filtration. The residue was washed with dichloromethane and the combined organic extracts were dried ($MgSO_4$). The mixture was distilled at reduced pressure to yield the epoxide.

1-(1,1,2,3,3,3-Hexafluoropropyl)cyclopentene oxide 44. 1-(1,1,2,3,3,3-Hexafluoropropyl)cyclopentene **36** (3.0 g, 14 mmol) and *m*-chloroperbenzoic acid (4.8 g, 28 mmol) gave *1-(1,1,2,3,3,3-hexafluoropropyl)cyclopentene oxide* **44** (2.0 g, 61%) as a colourless liquid and as a mixture of diastereoisomers; bp 147–148 °C (Found: C, 40.9; H, 3.5. $C_8H_8F_6O$ requires C, 41.0; H, 3.4%); δ_H 1.4–2.2 (6 H, m, CH_2), 3.75 (1 H, m, H-2), 4.92 (1 H, m, CFH); δ_C 19.17 (s, C-4), 25.20 (m, C-5), 26.28 (s, C-3), 61.60 (d, $^3J_{CF}$ 6.5, C-2), 64.96 (t, $^2J_{CF}$ 33.6, C-1), 84.49 (m, CFH), 115.38 (ddd, $^1J_{CF1}$ 262, $^1J_{CF2}$ 250, $^2J_{CF}$ 25.1, CF_2), 120.54 (qd, $^1J_{CF}$ 283, $^2J_{CF}$ 25.5, CF_3); δ_F −74.15 (3 F, m, CF_3), −114.96 and −121.60 (2 F, AB, J_{AB} 274, CF_2), −210.83 (1 F, m, CFH); *m*/*z* (EI^+) 233 (40%), 205 (23), 199 (20), 159 (16), 67 (100).

1-(1,1,2,3,3,3-Hexafluoropropyl)cyclohexene oxide 45. 1-(1,1,2,3,3,3-Hexafluoropropyl)cyclohexene **37** (3.0 g, 13 mmol) and *m*-chloroperbenzoic acid (4.6 g, 27 mmol) gave *1-(1,1,2,3,3,3-hexafluoropropyl)cyclohexene oxide* **45** (2.2 g, 66%) as a colourless liquid and as a mixture of diastereoisomers; bp 168–170 °C (Found: C, 43.6; H, 4.0. $C_9H_{10}F_6O$ requires C, 43.5; H, 4.0%); δ_H 1.1–1.5 (4 H, m, H-4,5), 1.7–2.1 (4 H, m, H-2,6), 3.25–3.4 (1 H, m, H-2), 4.90 (1 H, m, CFH); δ_C 18.28 (s, C-4), 19.11 (s, C-5), 22.69 (s, C-6), 23.51 (s, C-3), 55.10 (dd, $^3J_{CF1}$ 9.2, $^3J_{CF2}$ 1.9, C-2), 58.04 (dd, $^2J_{CF1}$ 30.2, $^2J_{CF2}$ 24.4, C-1), 84.66 (m, CFH), 115.57 (ddd, $^1J_{CF1}$ 256, $^1J_{CF2}$ 251, $^2J_{CF}$ 24.8, CF_2), 120.43 (qd, $^1J_{CF}$ 282, $^2J_{CF}$ 25.5, CF_3); δ_F −74.38 (3 F, m, CF_3), −120.92 and −123.70 (2 F, AB J_{AB}, 271, CF_2), −211.02 (1 F, dq, $^2J_{HF}$ 44.4, $^3J_{FF}$ 10.9, CFH); *m*/*z* (EI^+) 233 (10%), 97 (45), 77 (16), 41 (100).

Dehydrogenation—general procedure

A quartz Carius tube (*ca.* 20 ml) charged with the alkene or diene and sulfur was degassed and sealed under vacuum. The tube was heated at 225 °C for 24 hours, cooled and opened. Hydrogen sulfide was allowed to evaporate through a scrubber, and the remaining liquid was purified by transfer under vacuum to give the aromatic derivative as a colourless, clear liquid.

1-(1,1,2,3,3,3-Hexafluoropropyl)benzene 46. 1-(1,1,2,3,3,3-Hexafluoropropyl)cyclohexene **37** (0.8 g, 3.5 mmol) and sulfur (0.3 g, 10 mmol) gave *1-(1,1,2,3,3,3-hexafluoropropyl)benzene* **46** (0.7 g, 88%); bp 140–142 °C (Found: C, 47.1; H, 2.7; $[M]^+$, 228.0377. $C_9H_6F_6$ requires C, 47.4; H, 2.6%; $[M]^+$, 228.0374); δ_H 4.86 (1 H, dm, $^2J_{HF}$ 43.6, CFH), 7.43 (5 H, m, Ar-H); δ_C 86.97 (dm, $^1J_{CF}$ 199, CFH), 117.15 (m, CF_2), 117.74 (qm, $^1J_{CF}$ 249, CF_3), 125.81 (t, $^3J_{CF}$ 6.1, C-2), 128.67 (s, C-4), 130.10 (s, C-3), 131.31 (t, $^2J_{CF}$ 30.1, C-1); δ_F −73.86 (3 F, m, CF_3), −104.14 and −109.97 (2 F, AB, J_{AB} 282, CF_2), −208.88 (1 F, dm, $^2J_{HF}$ 43.6, CFH); *m*/*z* (EI^+) 228 (M^+, 18%), 127 (100), 77 (30), 69 (15).

1,4-Bis(1,1,2,3,3,3-hexafluoropropyl)benzene 47. A mixture of 1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexa-1,3-diene **39** and 1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexa-1,4-diene **40** (1.3 g, 3.4 mmol) and sulfur (0.24 g, 7.5 mmol) gave *1,4-bis(1,1,2,3,3,3-hexafluoropropyl)benzene* **47** (0.7 g, 88%) as a colourless liquid and as a mixture of diastereoisomers; bp 188 °C (Found: C, 37.8; H, 1.4. $C_{12}H_6F_{12}$ requires C, 38.1; H, 1.6%); δ_H 5.96 (1 H, dm, $^2J_{HF}$ 44.0, CFH), 7.5–8.0 (2 H, m, Ar-H); δ_C 87.25 (dm, $^1J_{CF}$ 195.1, CFH), 117.61 (td, $^1J_{CF}$ 249.4, $^2J_{CF}$ 23.7, CF_2), 121.94 (qd, $^1J_{CF}$ 281.6, $^2J_{CF}$ 26.2, CF_3), 126.77 (t, $^3J_{CF}$ 6.5, C-2), 135.86 (t, $^2J_{CF}$ 24.8, C-1); δ_F −74.59 (3 F, m, CF_3), −106.46 and −110.75 (2 F, AB, J_{AB} 267.5, CF_2), −211.75 (1 F, dm, $^2J_{HF}$ 41.4, CFH); *m*/*z* (EI^+) 378 (M^+, 10%), 277 (100), 189 (16), 176 (84), 126 (13).

X-Ray crystallography

Single-crystals for X-ray diffraction studies were obtained from acetone. The experiments were carried out with a SMART 1K CCD area detector (mounted on a 3-circle diffractometer), using graphite-monochromated Mo-Kα radiation. A combination of four sets of ω scans (each scan of 0.3°), each set at different φ and/or 2θ angle positions, nominally covered over a hemisphere of reciprocal space. Reflection intensities were integrated using SAINT software[24] and corrected for Lorentz and polarisation factors. For **25**, the experiment was carried out on a Rigaku AFC6S 4-circle diffractometer ($2\theta/\omega$ scan mode), using graphite-monochromated Cu-Kα radiation. Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostats were used for low-temperature experiments. Crystal data and experimental details are listed in Table 3. The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all reflections, using SHELXTL software.[25] In **19**, C and O atoms were refined in an anisotropic, and all H atoms in isotropic, approximation. In **23**, **24** and **25**/aldol, ordered non-H atoms were refined anisotropically, disordered ones isotropically, with H atoms 'riding'. In **25**, due to a relatively small number of observed reflections, only the F, O and outer C atoms were refined anisotropically, the ring C atoms in isotropic approximation. In all structures (except **19**) direct location of hydroxy H atoms was difficult; thus the torsion angles around the C–O bonds were optimised, taking into account both the difference electron density map and the possibilities of hydrogen bonding; subsequently these hydrogens were treated in riding model. CCDC reference number 207/409. See http://

Table 3 Crystal data

Compound	**19**	**23**	**24**	**25**	**25**/aldol
Formula	$C_6H_{12}O_2$	$C_{11}H_{10}F_{12}O_2$	$C_{12}H_{12}F_{12}O_2$	$C_{12}H_{12}F_{12}O_2$	$3C_{12}H_{12}F_{12}O_2{\cdot}2C_6H_{12}O_2$
Formula weight	116.16	402.19	416.22	416.22	1480.96
T/K	295	150	150	150	150
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
a/Å	6.374(1)	12.651(1)	10.590(2)	14.673(2)	10.709(4)
b/Å	21.313(5)	10.436(1)	39.347(3)	10.801(2)	10.853(3)
c/Å	7.328(2)	22.301(2)	15.135(5)	18.882(2)	13.926(4)
α (°)	90	90	90	90	106.98(1)
β (°)	95.86(1)	103.69(1)	94.60(1)	90.90(1)	99.83(2)
γ (°)	90	90	90	90	91.33(1)
V/Å^3	990.3(4)	2860.7(4)	6286(3)	2992.1(7)	1520.7(8)
Space group	$P2_1/n$ (# 14)	$P2_1/n$ (# 14)	$P2_1/n$ (# 14)	Pn (# 7)	$P\bar{1}$ (# 2)
Z	6	8	16	8	1
λ/Å	0.71073	0.71073	0.71073	1.54184	0.71073
μ/mm^{-1}	0.09	0.23	0.21	2.05	0.18
Density calc./g cm^{-3}	1.17	1.87	1.76	1.85	1.62
Reflections total	5886	16913	37884	5205	9023
Max. 2θ (°)	50	50	50	150	50
Unique refls.	1713	4845	10676	4771	5331
Refls. with $I > 2\sigma(I)$	1191	2747	6678	3201	3702
R_{int}	0.060	0.107	0.129	0.062	0.113
No. of variables	182	473	858	666	461
w$R(F^2)$, all data	0.113	0.203	0.378	0.341	0.240
$R[I > 2\sigma(I)]$	0.048	0.094	0.142	0.137	0.094
$\Delta\rho_{max,min}$/e Å^{-3}	0.12, −0.14	0.55, −0.40	0.85, −0.46	1.58, −0.66	0.49, −0.38

www.rsc.org/suppdata/p1/a9/a909778c for crystallographic files in .cif format.

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