Free radical chemistry. Part 10.[1] Addition of acyclic and cyclic alkanes to hexafluoropropene

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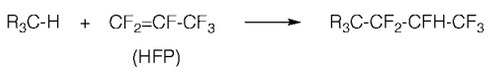
γ-Ray or peroxide initiated reactions of acyclic and cyclic alkanes with hexafluoropropene are described. A variety of perfluorocarbons and polyfluorinated alkenes, di-enes and a tetra-ene were synthesised from these polyfluoroalkylated alkanes. Elimination of hydrogen fluoride gives fluorinated alkenes, with unusual kinetic control of product formation and further fluorinations gave novel perfluorocarbons. X-Ray crystallography established structures of some isomers and NMR spectroscopy was used principally to establish the structures of others.

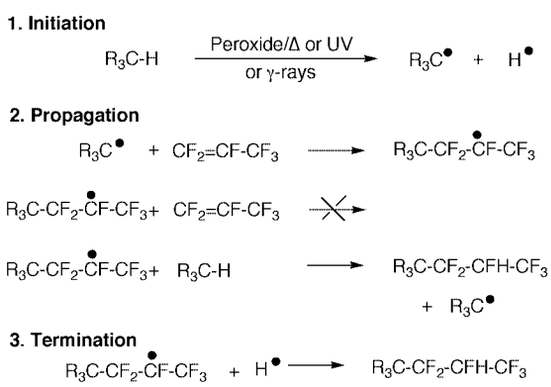
Introduction

We have a continued interest in the carbon–hydrogen bond as a functional group for reactions with unsaturated fluorine-containing compounds because, in principle, this is a potentially versatile route to a variety of fluorine containing intermediates and here we apply this approach to hydrocarbons. Many workers have directed considerable effort toward the general process of functionalising hydrocarbons,[2–4] with varying success, but here we will demonstrate that formation of carbon–carbon bonds, by reactions of hydrocarbons with fluorinated alkenes, is an effective process, Scheme 1.



Scheme 1

The area is still undeveloped, although some work has been reported by Haszeldine and co-workers[5–7] and by workers in the former Soviet Union.[8–10] Reactions that we will describe, involve the familiar radical chain processes, Scheme 2, where



Scheme 2

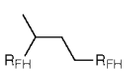
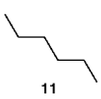
for *initiation* we have employed both peroxide and γ-ray induced procedures and these give very similar results, for reactions that are conducted at the same temperatures although, for much of our work γ-ray induced reactions were carried out at room temperature where greater selectivity can be achieved. It is worth emphasising, with regard to *propagation*, that radicals derived from hydrocarbons are relatively *nucleophilic* and fluorinated alkenes are, of course, extremely *electrophilic* in character and, as a consequence of these polar influences, we have very favourable circumstances for reactivity. [Perhaps more appropriately, we should refer to radicals with high SOMO energies, rather than *nucleophilic* radicals, reacting with alkenes of low LUMO energy, rather than *electrophilic* alkenes, *etc.*[11] However, we have used 'philicity' terminology, represented in Schemes by δ^+, δ^- *etc.*, throughout, merely for simplicity of presentation.] Indeed, the importance of radical polarity in influencing reactivities is being increasingly recognised[12] and we have drawn attention to the importance of such effects in earlier parts of this series.[13] Dolbier has also drawn attention to the importance of polar effects in reactions of fluorinated radicals with alkenes.[14] Premature *chain termination* can, of course, be a feature that limits yields and trace amounts of impurities (sometimes not easily detectable) may act as inhibitors. This makes separate qualitative comparisons of reactivity based on yields very capricious and our approach to circumventing this problem, is to carry out competition reactions between various substrates (see later).

We have used hexafluoropropene (HFP) especially because it does not readily homopolymerise and therefore, the reactions described in this paper provide a route to polyfluoro-*n*-propyl derivatives and consequently to the further chemistry that can be performed with these derivatives, which we will describe here and in forthcoming publications.

Results and discussion

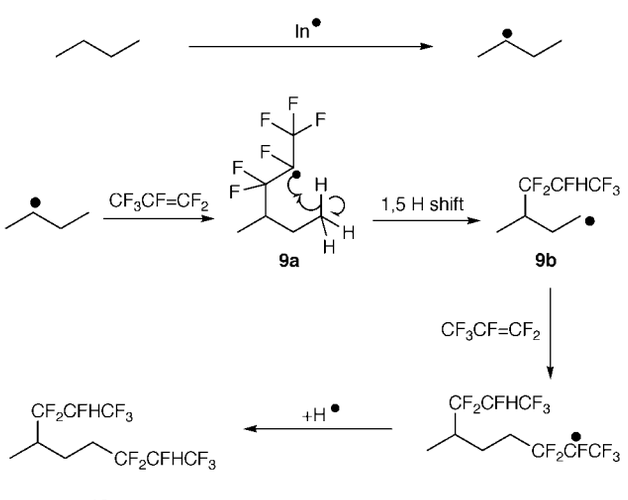
Starting with acyclic systems, various reactions are summarised in Table 1; we were unable to effect reaction with methane, even at 140 °C, but propane reacted readily even at room temperature, showing a strong preference for the secondary site. However, it is interesting to note that *n*-butane gave the di-adduct **10** as the principal product and that the second addition occurred *exclusively at the primary site*; we will return to this point later. It is important to emphasise that using γ-rays for initiation, the *conversions* noted in Table 1 are quite modest but this is not significant because *yields* are essentially

Table 1 Addition of acyclic hydrocarbons to HFP

Alkane	Alkane–HFP	Initiator	Major products (R_{FH} = CF_2CFHCF_3) and conversions (calculated based on alkane)
CH_4 **1**	1 : 1	DTBP (di-*tert*-butyl peroxide)	No reaction
 **2**	1 : 1.2	γ-rays	 **3** 19%  **4** 1%
	1 : 1.5	DTBP	**3** 75% **4** 3%
 **5**	1 : 2	γ-rays	 **6** 42%  **7**
	1 : 1.3	DTBP	**6** 80% **7** 3%
 **8**	1 : 2	γ-rays	 **9** 6%  **10** 11%
 **11**	1 : 2	DTBP	 **12** 1%  **13** 8%  **14** 5%

quantitative and, of course, conversions may be increased with time and/or temperature.

Formation of the di-adduct **10** shown in Table 1, involves preferential attack at the primary site for introduction of the second group, and constitutes clear evidence for what is now a well-established sequence in free-radical reactions.[13–15] That is, that radical **9a**, Scheme 3, formed by addition of HFP to



Scheme 3

n-butane, has the opportunity to abstract a hydrogen from the chain in a 'back-biting' process, *via* a strain-free six membered ring transition state; this is obviously in preference to a five membered ring transition state and appears to be the basis for preferential attack at the primary site in the intramolecular step, leading to the formation of **10**. It is useful to emphasise that this *intramolecular* process obviously proceeds readily whereas, in contrast, we shall note later that introduction of one hexafluoro-*n*-propyl group *deactivates* the system to further reaction with hexafluoropropene to form di-adducts by a bi-molecular process.

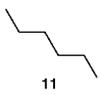
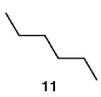
The structures of these and subsequent systems followed principally from NMR spectra, although some examples of single-crystal X-ray studies place our assignments on a firm basis. Regioselective addition to the difluoromethylene group of HFP occurs, in most cases, although 1–3% of the opposite isomers have been detected, depending on the system and the reaction conditions.

The majority of the product from propane with HFP arises from addition to the methylene carbon rather than to the methyl sites. This is confirmed by the ^{1}H NMR spectrum of the product **3** which displayed three resonances in a 6 : 1 : 1 ratio having chemical shifts appropriate to methyl, methine and CFH hydrogens respectively. Similarly, addition of 2-methylpropane **5** to HFP proceeds mainly *via* the methine carbon to give the major product **6**, confirmed by the two resonances in its simple ^{1}H NMR spectrum, in a ratio of 9 : 1 which have chemical shifts consistent with methyl and CFH hydrogens respectively. The mono-addition product **9** arises from addition of butane to HFP *via* the methylene carbon, confirmed by the ^{1}H NMR spectrum of **9** which has six resonances. The two large resonances at high field are characteristic of the two methyl groups which have remained intact. The CFH and methine groups are multiplets shifted to low field, as expected, and separate resonances are observed for the two methylene hydrogens due to their diastereotopic nature. The structure of the di-adduct **10** was confirmed by its ^{13}C NMR spectrum. There are four resonances in the high field region, indicating that the second addition step occurred *via* the terminal methyl, rather than a methylene group, which would have led to a product with fewer resonances than are observed. In comparison with the ^{1}H NMR spectrum of the mono-adduct **9**, which has two methyl resonances, the ^{1}H NMR spectrum of **10** has only one methyl resonance. Similar logic was used to deduce the structures of other systems.

In competition reactions we explored the effect of containment in a ring on the reactivity of C–H bonds and the results are shown in Table 2. Relative reactivities are statistically corrected for the number of sites available and we may conclude that containment in a ring has no major effect on overall reactivity. However, the intramolecular processes *e.g.* as illustrated in Scheme 3, that lead to multi-substitution products, are probably absent in the cyclic systems.

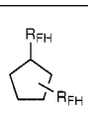
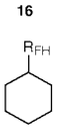
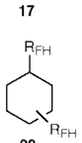
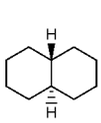
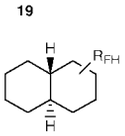
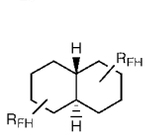
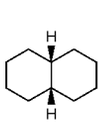
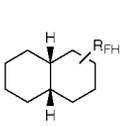
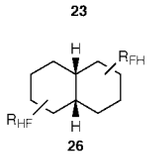
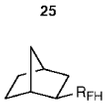
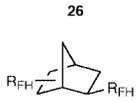
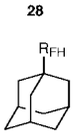
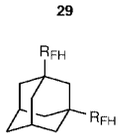
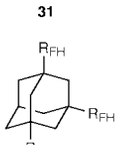
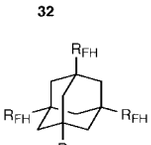
Returning to preparative-scale reactions, products from cyclohexane are shown in Table 3, where very high yields of products are recovered and the ratio of mono- to di-addition products depends on the ratio of HFP to cyclohexane, and on temperature. Points to note are that a diastereomer of the 1,4-di-adduct **20** crystallised from the di-adduct mixture on cooling and a single crystal X-ray structure of this compound was

Table 2 Competition reactions between acyclic and cyclic hydrocarbons

Hydrocarbon	Hydrocarbon[a] ratio after reaction (R_1)	Hydrocarbon[a] ratio prior to reaction (R_2)	$R_1 - R_2$	Overall relative reactivities	Relative reactivities per CH_2 site
 11	47.07	38.50	8.57	1.48	0.37
 15	44.60	38.81	5.79	1	0.2
 11	48.42	10.5	37.92	1.03	0.26
 18	48.56	11.7	36.86	1	0.17

[a] GLC peak areas.

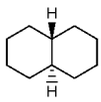
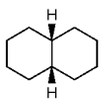
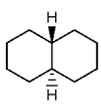
Table 3 Addition of cyclic hydrocarbons to HFP

R–H	R–H : HFP	Initiator	Conversion of R–H (%)	Major products and yields (%) ($R_{FH} = CF_2CFHCF_3$)			
 15	1 : 1.6	γ-rays	54	 16	86	 17	9
	1 : 2	DTBP	100		57		23
 18	1 : 1.5	γ-rays	79	 19	90	 20	4
	1 : 2	DTBP	99		39		53
 21	1 : 2	γ-rays		 22	5	 23	—
	1 : 1.5	DTBP	79		51		27
 24	1 : 2	γ-rays		 25	5	 26	—
	1 : 2	DTBP	39		56		33
 27	1 : 1.3	γ-rays	65	 28	80	 29	12
	1 : 1.4	DTBP	100		45		37
 30	1 : 1.2	DTBP	92	 31	60	 32	19
 30	1 : 7	DTBP	100	 33	59	 34	36

determined (see later). Also the 1,3- : 1,4- di-adduct ratio is *ca.* 2 : 1 and this statistical distribution implies that the deactivating effect of the hexafluoropropyl group decreases rapidly with distance in this system, because no 1,2-di-adduct was detected.

Reactions with *cis*- and *trans*-decalins (decahydronaphthalene) gave mixtures containing isomeric mono- and di-adducts in each case, but we were unable to separate these mixtures and the spectra were too complex to form firm conclusions. However, elimination of hydrogen fluoride from the mono-adduct mixture (see later) led to a considerable simplification of the ^{13}C NMR spectra, which enabled us to conclude that negligible attack had occurred at the tertiary sites

Table 4 Competition reactions between cyclic hydrocarbons

Hydrocarbon	Hydrocarbon[a] ratio prior to reaction (R_1)	Hydrocarbon[a] ratio after reaction (R_2)	$R_1 - R_2$	Overall reactivities	Relative reactivity per C–H site
 **21**	47.82	43.69	4.13/18	1	1
 **24**	52.18	43.12	9.06/18	2.19	2.19
 **21**	53.41	49.75	3.66/18	1	(0.06) 1
 **18**	46.58	34.46	12.12/12	3.31	(0.28) 4.7
 **15**	45.13	36.94	8.19/10	1	(0.2) 1
 **18**	54.76	44.54	10.22/12	1.24	(0.21) 1.05

[a] GLC peak areas.

and, most obviously, this is a manifestation of steric effects. Although we were unable to detect impurities in either sample of *cis*- or *trans*-decalin, under the same conditions conversion to products with HFP varied considerably (*cis*- : *trans*- = 39 : 79) whereas in a competition reaction, there was little discernible difference in reactivity (see Table 4). The notable conclusion from the other results from competition experiments contained in Table 4, is that there is comparatively little difference in relative reactivity for these various ring systems.

Attack on norbornane (bicyclo[2.2.1]heptane) gave mainly 2-substitution, *i.e.* at the secondary site, **28**, **29** Table 3, and there was no evidence for attack at the tertiary site. Even the di-adducts **29** contained no products arising from attack at a tertiary site and the ratio of the 2,5- : 2,6-isomers in **29** is *ca.* 2 : 1. These results parallel other processes involving radical attack on norbornane,[16] but we are unaware of convincing arguments advanced to account for the absence of radical attack at the tertiary site, although an obvious point is the effect of strain. Increased ring strain in the norbornyl system will lead to a greater amount of s-character in the bridgehead carbon–hydrogen bond, than in unstrained sp^3 systems and this extra s-character (less nucleophilic) could account for the reluctance to react *via* a bridgehead position.

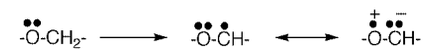
In contrast to norbornane, adamantane reacts almost exclusively at the tertiary sites, giving **31**–**34**, and the product distribution depends on conditions. The bridgehead position in adamantane is unstrained and therefore is more favourable to hydrogen abstraction than in the norbornyl system, indeed, remarkably so and even a tetra-adduct is formed. Furthermore, this tetra-adduct **34** was easily obtained pure because it crystallised from the adduct mixture when dissolved in hexane or chloroform.

We have compared reactivities of hydrocarbons with those of corresponding ethers, Table 5, where adjacent oxygen is known to encourage the formation of adjacent radical centres, Scheme 4. Surprisingly, there is little overall difference, although

Table 5 Competition reactions between hydrocarbons and ethers (γ-rays, RT)

	Ratio prior to[a] reaction (R_1)	Ratio after[a] reaction (R_2)	$(R_1 - R_2)$	Relative reactivity per CH site attacked
 **18**	58.92	44.38	14.54	1.21 (12 Sites)
 **35**	41.08	29.50	11.58	2.9 (4 sites)
 **36**			No reaction	
 **37**			Reacted exclusively	

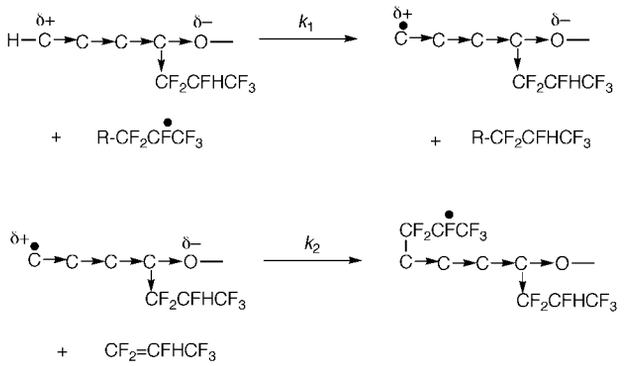
[a] GLC peak areas.



Scheme 4

attack occurs exclusively adjacent to oxygen in the ethers and these sites are probably slightly *activated*, with respect to cyclohexane. However, we can also conclude that the sites remote from the oxygen in the ether are *deactivated* with respect to the corresponding hydrocarbon. A comparison between tetrahydrofuran **37** and the mono-adduct **36** demonstrates clearly the deactivating effect of the hexafluoro-*n*-propyl group on *all* of the remaining sites in **36**, including the position adjacent to

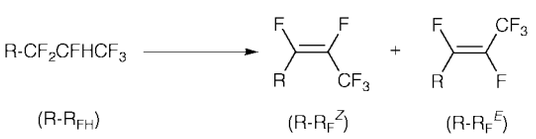
oxygen. This is undoubtedly due to polar effects, arising from the introduction of the electron withdrawing hexafluoro-*n*-propyl group which makes it more difficult for an *electrophilic* radical to abstract a hydrogen atom, from the more electrophilic centre. Therefore both of the propagation steps k_1, k_2, Scheme 5, are inhibited after introduction of the first fluorinated group.



Scheme 5

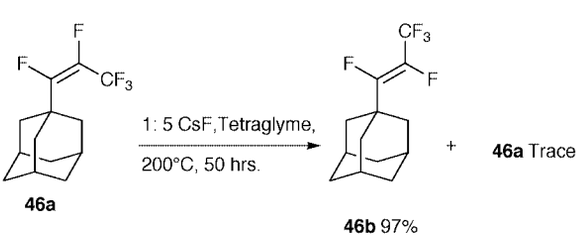
Eliminations of hydrogen fluoride

An obvious way of further functionalisation of these systems is the elimination of hydrogen fluoride, giving new fluorinated alkene derivatives, Scheme 6. These are, of course potential



Scheme 6

'building blocks' for incorporation of fluorine into more complex molecules and after exploring a variety of approaches, we adopted the procedure of adding the reactant to potassium *tert*-butoxide in ether, while cooling. Yields of various products are shown in Table 6 but, what is quite remarkable, is that the *Z*-isomer, *i.e.* with the fluorine atoms *syn*- in the alkene, are formed *preferentially*. This is especially surprising in the case of the adamantane adduct where, at 0 °C, the *Z*-isomer is obtained almost *exclusively*, while the *E*-isomer is obtained at higher temperatures. Obviously, kinetic control is leading to the *Z*-isomer and we have confirmed that the *Z*-isomer is converted to the *E*-isomer by heating with caesium fluoride in tetraglyme at 200 °C in a sealed tube, Scheme 7.



Scheme 7

The question then arises as to what the factors might be that lead to the *Z*-isomer. It is probable that the mechanism of elimination is either E1cB or E1cB-like and, indeed, we have demonstrated that in reaction with **31**, recovered starting material contained *ca.* 9% deuterium, **31a**, when the reaction was carried out with ^{t}BuOD, after *ca.* 50% conversion to product **46b**, Scheme 8. *anti*-Elimination is most likely, and therefore we need to account for why a transition-state that resembles (A) is more favourable than one that resembles (B) (Fig. 1). Clearly, for this situation to arise, there must be some energy-lowering interaction between R and trifluoromethyl, *e.g.* hydrogen bond-

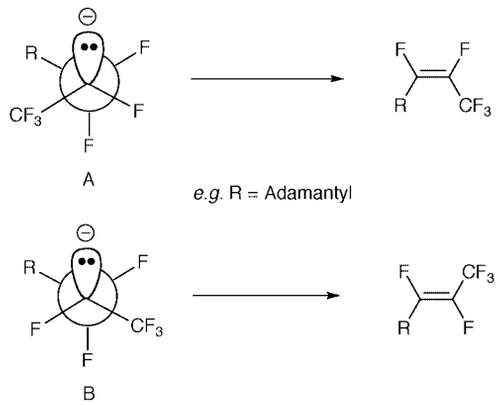


Fig. 1 Possible transition states for E1cB elimination.

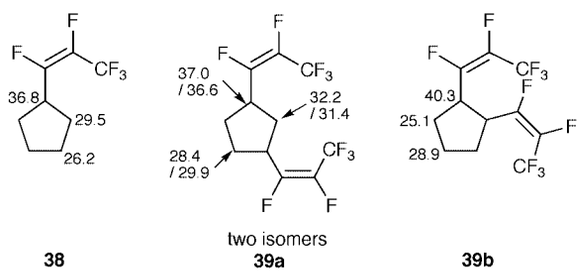
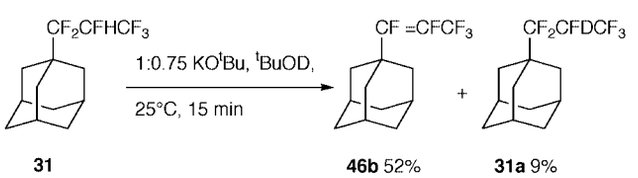


Fig. 2 ^{13}C NMR chemical shifts (ppm) of pentafluoropropenylcyclopentane systems **38** and **39**.



Scheme 8

ing in the *carbanion-like* transition-state. We can only probe this situation by calculations, and these are proceeding in the hands of other workers.[17]

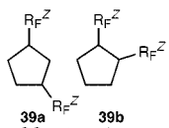
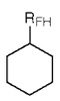
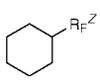
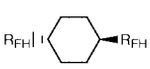
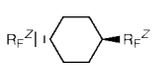
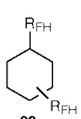
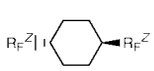
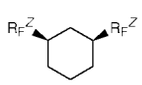
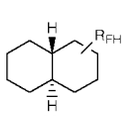
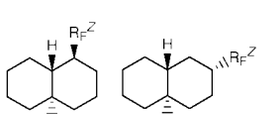
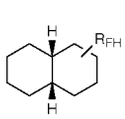
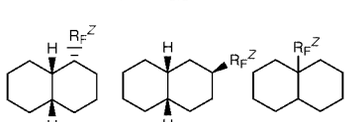
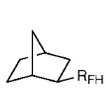
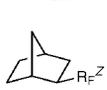
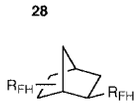
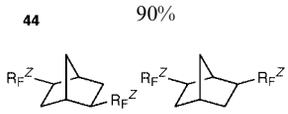
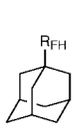
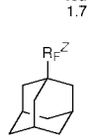
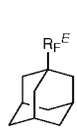
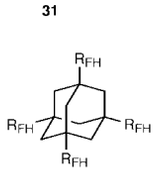
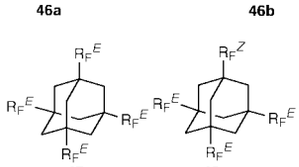
Structure elucidation of cyclic systems

Elimination of hydrogen fluoride at low temperatures to give only the *Z*-isomer in many cases, not only greatly simplifies the product mixtures, by eliminating a chiral centre, but also allows fuller characterisation of hexafluoropropyl adducts because of their simplified NMR spectra.

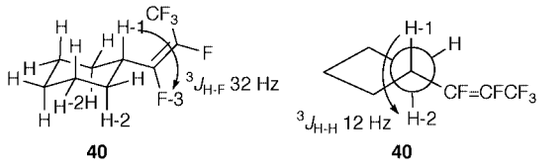
Chemical shifts of *Z*-pentafluoropropenylcyclopentane **38** were used as a model for the structure elucidation of the analogous di-enes **39a**,**b**. Three components were found in the di-ene mixture **39** and by comparing the broad band proton decoupled ^{13}C NMR spectrum of the mixture with the mono-ene **38**, two of the components were assigned as the 1,3-substituted system **39a** and the other as the 1,2-substituted cyclopentane **39b**, Fig. 2. However, it was not possible to assign either of isomers **39a**,**b**, as *cis*- and *trans*- with respect to the cyclopentane.

Z-Pentafluoropropenylcyclohexane **40** was investigated fully due to its applicability as a model compound for many of the other systems. The ^{19}F and ^{1}H NMR spectra of dehydrofluorinated product **40** show antiperiplanar F-3–H-1 coupling, which is quite large, giving a doublet *ca.* 32 Hz, Fig. 3. This coupling is also evident in the cyclopentyl system **38**, the norbornyl system **44** and the *trans*- **42** and *cis*-decalin **43a** and **43b** systems, demonstrating that these systems are also formed by attack on HFP *via* radicals derived from secondary sites in the corresponding hydrocarbons. Conversely, the absence of analogous coupling is diagnostic of products that are derived from attack through tertiary sites in the hydrocarbon, as in the adamantyl systems **46**–**48**.

Table 6 Dehydrofluorination of cyclic hexafluoropropyl adducts (see Scheme 6, for R_F^Z, R_F^E)

$R–R_{FH}$	Conditions	Yields (%)
 **16**	KO^{t}Bu, −78 °C	 **38** 75%
 **17**	KO^{t}Bu, −78 °C	 **39a** 6.3 : **39b** 1 60%
 **19**	KO^{t}Bu, 0 °C	 **40** 92%
 **20a**	KO^{t}Bu, −10 °C	 **41a** 67%
 **20**	KO^{t}Bu, −10 °C	 **41a** 30%  **41b** 57%
 **22**	KO^{t}Bu, −10 °C	 **42a** 1 : **42b** 3.3 82%
 **25**	KO^{t}Bu, −10 °C	 **43a** 2.5 : **43b** 2.9 : **43c** 1 85%
 **28**	KO^{t}Bu, −10 °C	 **44** 90%
 **29**	KO^{t}Bu, −10 °C	 **45a** 1.7 : **45b** 1 93%
 **31**	KO^{t}Bu, RT KO^{t}Bu, −10 °C	 **46a** trace 90% 85%  **46b** trace
 **34**	KO^{t}Bu, RT	 **47** 7 : **48** 1 78%

Further analysis of the vicinal coupling to H-1 in the ^{1}H NMR spectrum of *Z*-pentafluoropropenylcyclohexane **40** gives additional useful stereochemical information which can be applied to other similar systems. If, as expected, the fluoroalkenyl group occupies an equatorial position about the cyclohexyl ring, H-1–H-2 antiperiplanar vicinal coupling of *ca.* 12 Hz should be evident (see Fig. 3) which would not occur if the substituent were axial. In fact, we observe this coupling as a triplet (J_{HH} 12 Hz) due to the two equivalent H-2 hydrogens coupling to H-1 in this manner. We observe similar coupling in other systems containing six-membered rings such as the mono-ene derivatives of *trans*-, **42a**, **42b** and *cis*-decalin **43a** and **43b** and the di-ene derivatives of cyclohexane **41a**, Table 6, confirming that the fluoroalkenyl group also occupies equatorial positions in each of these systems.



40 40

Fig. 3 Antiperiplanar coupling in *Z*-pentafluoropropenylcyclohexane **40**.

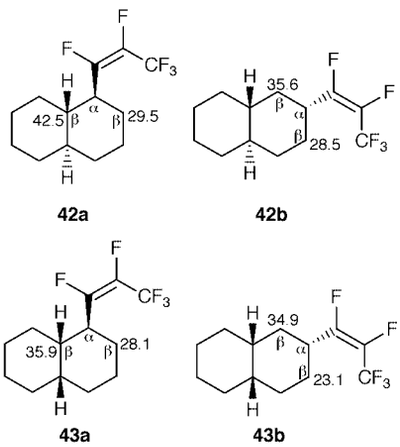


Fig. 4 ^{13}C NMR chemical shifts (ppm) of the sites β to fluoroalkylation in *trans*- and *cis*-decalins.

The di-enes derived from cyclohexane could be separated by crystallisation. The crystalline *trans*-1,4-bis(pentafluoroprop-1-enyl)cyclohexane **41a** was identified by its simple NMR spectra, due to its two-fold symmetry and a crystal structure confirmed these findings. The structure of *cis*-1,3-bis(pentafluoroprop-1-enyl)cyclohexane **41b** was established *via* a broad band proton decoupled ^{13}C NMR experiment. Four resonances were observed at high field which were attributable to the cyclohexane ring and this confirmed the ring to be 1,3-substituted as 1,2- or 1,4-substitution would give three or two resonances in the high field region, respectively.

The regiochemistry of *Z*-pentafluoropropenyl derivatives **42a**, **42b**, of *trans*-decalin, was defined by the broad band proton decoupled ^{13}C NMR and ^{13}C DEPT NMR spectra of the mixture; specifically, by analysis of the β-positions to the site of fluoroalkylation, Fig. 4. The ^{13}C DEPT NMR spectrum identified three methylene carbons, at 35.6, 29.5 and 28.5 ppm, as doublets ($^3J_{CF}$ *ca.* 3 Hz). The doublet at lowest field was assigned to the 1-position of the 2-isomer **42b** due to the increased deshielding effect of the adjacent bridgehead position, whereas the doublet at lowest field was assigned to the 3-position, due to its remoteness from the bridgehead site. The remaining doublet was therefore assigned to the 2-position of the 1-isomer **42a** and the bridgehead carbon at lowest field, 42.5 ppm, was assigned to the other β-site, due to the deshielding effect of the fluoroalkenyl group. A similar method was used to identify the regiochemistry of the two major components of (*Z*-pentafluoropropenyl)-*cis*-decalin **43a**, **43b**, Fig. 4.

It was confirmed that norbornane attacks HFP through a secondary site, *i.e.* at the 7- or 2-position, due to the observation of antiperiplanar vicinal coupling between its vinylic F-3 and a methine H-2, akin to the cyclohexane derivative **40** discussed earlier, and various NMR techniques were used to identify the stereochemistry of the product **44** more precisely. Seven resonances were observed in the high field region of the broad band proton decoupled ^{13}C NMR spectrum of the alkene **44**, eliminating the possibility of attack at the 7-position, due to the high symmetry. To determine whether the norbornyl system was *endo*- or *exo*-substituted at the 2-position, initially a ^{13}C DEPT NMR experiment was carried out, to identify the bridgehead carbons, and then a ^{13}C–^{1}H HETCOR NMR experiment con-

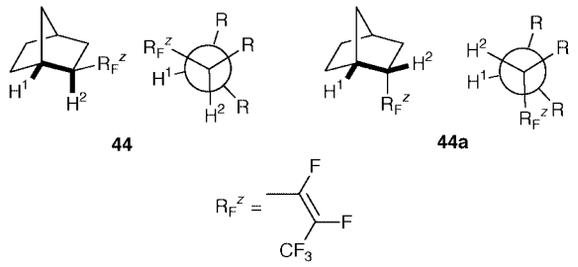


Fig. 5 Dihedral angles of *exo*- and *endo*-substituted norbornanes.

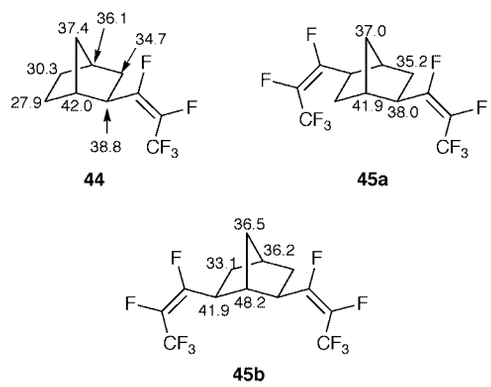


Fig. 6 ^{13}C NMR chemical shift assignments in the mono- and di-enes of norbornane.

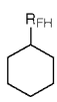
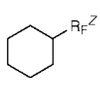
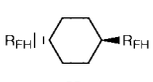
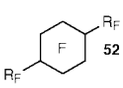
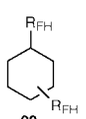
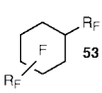
firmed which hydrogens were associated with these positions. Vicinal coupling (*J ca.* 6–8 Hz) between the tertiary hydrogen (H-1) and the hydrogen (H-2) at the adjacent position, Fig. 5, would be evident if the norbornyl system were *endo*-substituted, due to their dihedral angle of 30°, but if the product were *exo*-substituted no coupling would be observed, because of the dihedral angle being *ca.* 90°. In fact, a ^{1}H–^{1}H COSY NMR experiment determined that no coupling was evident between H-1 and H-2, confirming the product **44**, to be *exo*-substituted.

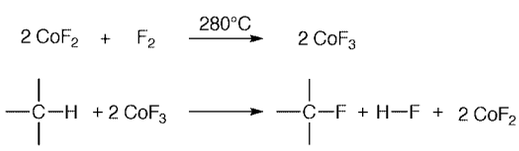
The NMR spectra of the norbornyl derivative **44** were used as models to elucidate the structures of the di-enes **45**. The ^{19}F NMR spectrum of the two component mixture revealed two sets of *syn*-fluorine signals, in a ratio of 1.7 : 1, suggesting that each di-ene contained equivalent *Z*-pentafluoropropenyl groups and therefore addition had only occurred at the *exo*-positions of the methylene groups in norbornane. The broad band proton decoupled ^{13}C NMR spectrum exhibited nine resonances in the 0–50 ppm region and a ^{13}C DEPT NMR spectrum identified five of them as methine carbons. Of these, two doublets at 38.0 ($^2J_{CF}$ = 21 Hz) and 39.9 ppm ($^2J_{CF}$ = 20 Hz) were assigned as the carbons attached to the perfluoroalkenyl groups and the remaining three as bridgehead carbons. A large doublet ($^2J_{CF}$ = 2.6 Hz) at 41.9 ppm was assigned as the bridgehead carbon in the di-ene **45a**, Fig. 6, because of its similar chemical shift to the analogous bridgehead of the mono-ene **44**. Singlets at 48.2 and 36.2 ppm were assigned as bridgehead carbons of di-ene **45b**. The lower field singlet was attributed to the bridgehead carbon between the two perfluoroalkenyl groups, because of the large deshielding from them and the higher field singlet was assigned to the other bridgehead carbon. The relative sizes of the ^{13}C NMR resonances indicate that the major component of the mixture was *exo*-2,5-bis[(1*Z*)-pentafluoroprop-1-enyl]norbornane **45a**.

Fluorination

Perfluorinated fluids are of increasing interest, for a variety of uses that include the 'fluoros-biphase' approach of Horvath[18] and co-workers and perfluorocarbons are made on the industrial scale by the use of cobalt trifluoride,[19] Scheme 9, because reaction with elemental fluorine directly, is usually too vigorous

Table 7 Cobalt trifluoride fluorinations ($R_{FH} = CF_2CFHCF_3$; $R_F = CF_2CF_2CF_3$)

	Temp./°C	Recovery	Major product (yield)	
 **16**	375	87%	 **49**	60%
 **17**	375	77%	 **50**	71%
 **19**	375	86%	 **51**	63%
 **40**	375	85%	 **51**	90%
 **20a**	400	77%	 **52**	65%
 **20**	375	83%	 **53**	58%



Scheme 9

and therefore, difficult to control. We have earlier demonstrated the benefit of introduction of a polyfluoroalkyl group because this moderates reactivity towards cobalt trifluoride, so that controlled reaction of both cobalt trifluoride and fluorine with ethers[20] and polyethers,[1] to obtain perfluorinated systems is possible. Here, we demonstrate a similar approach to synthesis of perfluorocarbons showing that a range of new systems may be obtained in this way. Examples of perfluorination are contained in Table 7.

X-Ray crystallographic studies

The crystal and molecular structures of *trans*-1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane **20a**, 1,3,5,7-tetrakis(1,1,2,3,3,3-hexafluoropropyl)adamantane **34**, and *trans*-1,4-bis[(1*Z*)-pentafluoroprop-1-enyl]cyclohexane **41a**, were determined by single crystal X-ray diffraction and confirmed unambiguously our assignments, some of which would be controversial without this complete evidence.

Molecule **20a** (see Table 6) is situated at a crystallographic inversion centre, Fig. 7, and is therefore a *meso*-isomer by its two asymmetric atoms C(5) and C(5′). The cyclohexane ring adopts a chair conformation with equatorial R_{FH} substituents.

Molecule **34** (Fig. 8) contains four asymmetric carbon atoms in the R_{FH} side-chains and therefore can exist in five different isomeric forms: *SSSS* and *RRRR*, *RSSS* and *SRRR*, and *RRSS*. Because of the similar sizes of hydrogen and fluorine atoms and conformational flexibility of the R_{FH} group, molecules (groups) with different configurations can occupy the same crystallographic site, giving rise to a sophisticated dis-

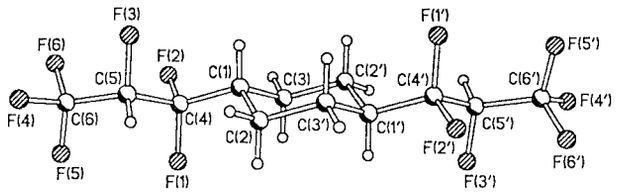


Fig. 7 X-Ray molecular structure of *trans*-1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane **20a**. Primed atoms are symmetrically related *via* an inversion centre.

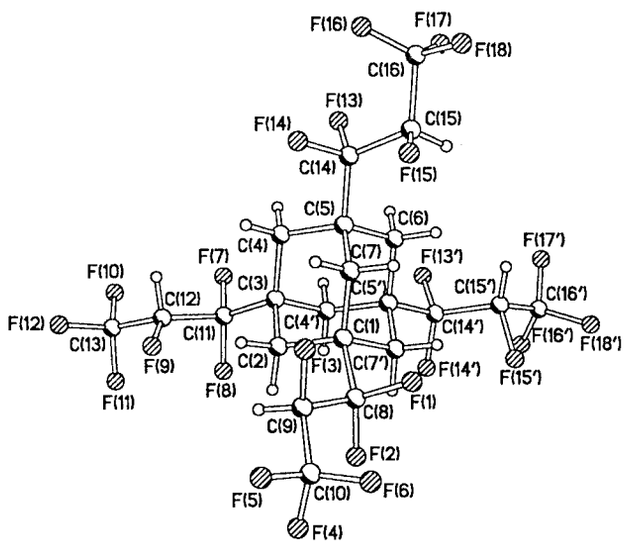


Fig. 8 X-Ray molecular structure of 1,3,5,7-tetrakis(1,1,2,3,3,3-hexafluoropropyl)adamantane **34**: one of the possible isomers (*RSSS*), the disorder is not shown. Primed atoms are symmetrically related *via* a mirror plane.

order. The molecule is located on a crystallographic mirror plane, passing through the atoms C(1), C(2), C(3) and C(6), but all four independent R_{FH} groups in the structure are disordered in different ways in the modes shown in Fig. 9. Thus all possible isomers may share the same crystallographic site, and since the space group is centrosymmetric (*Pnma*), the inversion equivalent of each isomer is also present. (An attempted structure solution in space group $Pna2_1$ revealed the same disorder, obviously conforming to the mirror symmetry). Crystals of **34** show small but significant variations of unit cell parameters, *e.g.* at room temperature, $a = 11.513(2)$ and 11.486(2), $b = 15.237(4)$ and 15.217(2), $c = 15.172(4)$ and 15.139(2) Å, respectively, for two specimens from different crystallisations. The difference may be due to uneven distribution of isomers.

Molecule **41a** (Fig. 10) possesses a crystallographic 2/*m* symmetry, with the C(1), C(3), C(4), C(5), F(1), F(2), F(4) and their equivalents lying in the mirror plane and the twofold axis passing through the midpoints of the C(2)–C(2″) and C(2′)–C(2‴) bonds. The cyclohexane ring adopts a chair conformation with equatorial orientation of the R_F^Z substituents. The configuration around the C(3)=C(4) bond is *cis*. The CF_3 group is disordered between two orientations (differing by a 180° rotation) with a 2 : 1 occupancy ratio. In either orientation, the F(4) atom lies in the mirror plane, while two other fluorine atoms, F(3) and F(3′), are related by this plane. However, high displacement parameters of these atoms may indicate further disorder.

Experimental

All starting materials were obtained commercially (Aldrich) and all solvents were dried using literature procedures. NMR spectra were recorded on either a Bruker AC 250, a Varian Gemini 200, Varian VXR400S or a Bruker AMX 500 spec-

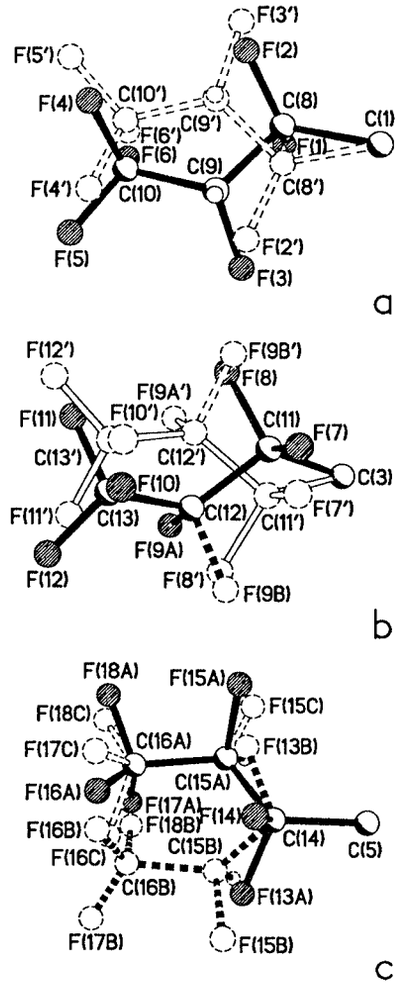


Fig. 9 Modes of disorder in RFH groups of **34**: (a) the two positions are related *via* a mirror plane; (b) the same, with each site shared by *R* and *S* configurations (A and B positions of F(9) have occupancies of 0.15 and 0.35, respectively); (c) symmetrically unrelated positions A (*S*) and B (*R*) have occupancies 0.7 and 0.3 respectively, with an additional rotational disorder of the former (position C, occupancy 0.2).

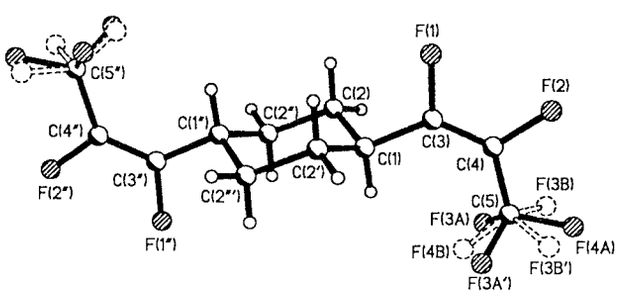


Fig. 10 X-Ray molecular structure of *trans*-1,4-bis[(1*Z*)-pentafluoroprop-1-enyl]cyclohexane **41a**. The CF_3 group is disordered over two positions with occupancies 2/3 (solid) and 1/3 (dashed). Primed atoms are related to the reference ones by *m* plane, double-primed by axis 2, triple-primed by the inversion centre.

trometer with tetramethylsilane and trichlorofluoromethane as standards. Spectral assignments were made with the aid of data collected by ^{13}C DEPT, ^{1}H–^{13}C HETCOR and ^{1}H–^{1}H COSY experiments and coupling constants are given in Hz. In ^{19}F NMR spectra, upfield shifts are quoted as negative. 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. Elemental analyses were obtained using either a Perkin-Elmer 240 or a Carlo Erba Elemental Analyser. Melting points were recorded at atmospheric pressure and are uncorrected. Distillations were carried out using either a Fischer Spahltroh MMS255 microdistillation apparatus or for higher boiling materials, a Buchi kugelrohr GKR-51 apparatus. Boiling points were recorded during the distillation or using the Siwoloboff method and superscript numbers given as part of boiling point data indicate the pressure (in mmHg) during measurement. Gas liquid Chromatography (GC) analyses were carried out using a Hewlett Packard 5890A gas liquid chromatograph equipped with a 25 m cross-linked methyl silicone capillary column. Preparative GC was performed on a Varian Aerograph Model 920 (catharometer detector) gas liquid chromatograph with packed columns, which was mainly a 3 m 10% SE 30. Gamma ray irradiations were performed in a purpose built shielded chamber with a cobalt-60 source (500 C original activity).

Radical addition reactions

General procedure. The reactions were carried out using sealed Pyrex tubes (for γ-ray initiation) or 150 ml and 250 ml autoclaves (for peroxide initiation). Liquid reagents were added to the tube/autoclave and degassed, then gaseous reagents were transferred *in vacuo*, using normal vacuum line techniques. The hydrocarbon substrate was usually used in a 1 : 1.5 deficiency to HFP. The tube/autoclave was sealed *in vacuo*, while cold (liquid air). For γ-initiation, the tube was irradiated at a fixed distance for varying periods, to give a total dose in the range 7–12 Mrad at room temperature. For thermal initiation using DTBP (di-*tert*-butyl peroxide) (at 1–5% w/w concentration) the autoclave was placed in a thermostatically controlled furnace for appropriate periods. The tube/autoclave was opened while the contents were cold (liquid air) and gaseous components were transferred *in vacuo* to a trap cooled in liquid air. Remaining liquid was distilled to give excess hydrocarbon substrate and products.

Methane (peroxide). Methane **1** (8.0 g, 0.5 mol), HFP (75.0 g, 0.5 mol) and DTBP (1.0 g, 6.8 mmol) were contained in a rocking autoclave at 140 °C for 24 h. Gaseous products were recovered to leave a small amount of liquid (*ca.* 3 ml), which on analysis by GC-MS gave no indication of the existence of the desired mono-adduct.

Propane (γ-rays). Propane **2** (2.3 g, 52 mmol) and HFP (9.0 g, 60 mmol) were irradiated for 8 days with γ-rays (12 Mrad) at room temperature. Gaseous components (9.0 g) were recovered to leave a colourless liquid, identified as an isomeric mixture of 4-methyl-1,1,1,2,3,3-hexafluoropentane **3** (1.9 g, 19%) and 1,1,1,2,3,3-hexafluorohexane **4** (0.1 g, 1%) bp 81–82 °C (Found: C, 37.4; H, 4.2. $C_6H_8F_6$ requires C, 37.1; H, 4.1%); 4-methyl-1,1,1,2,3,3-hexafluoropentane **3** δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.12 (6 H, m, CH_3), 2.34 (1 H, m, $CHCF_2$), 4.82 (1 H, dm, $^2J_{HF}$ 44, CHF); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −74.5 (3 F, m, CF_3), −117.7 and −121.8 (2 F, AB, J_{AB} 265, CF_2), −212.0 (1 F, d, $^2J_{HF}$ 27, CFH); *m*/*z* (EI^+) 175 (0.5%), 93 (46), 65 (72), 43 (100), 41 (86); 1,1,1,2,3,3-hexafluorohexane **4** δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.00 (3 H, m, CH_3), 1.58 (2 H, m, CH_2), 1.90 (2 H, m, CH_2CF_2), 4.82 (1 H, dm, $^2J_{HF}$ 44, CHF); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −74.5 (3 F, m, CF_3), −108.0 and −111.1 (2 F, AB, J_{AB} 269, CF_2), −211.0 (1 F, br s, CFH); *m*/*z* (EI^+) 175 (2%), 93 (54), 69 (58), 65 (100), 43 (94).

Propane (peroxide). Propane **2** (2.4 g, 55 mmol), HFP (12.7 g, 82 mmol) and DTBP (0.6 g, 4 mmol) were contained in a rocking autoclave at 140 °C for 24 h. Gaseous products (6.3 g) were recovered to leave a pale yellow liquid, which on fractional distillation (81–82 °C) gave an isomeric mixture of 4-methyl-1,1,1,2,3,3-hexafluoropentane **3** (7.9 g, 75%) and 1,1,1,2,3,3-hexafluorohexane **4** (0.4 g, 3%).

2-Methylpropane (γ-rays). 2-Methylpropane **5** (5.8 g, 0.1 mol) and HFP (30.0 g, 0.2 mol) were irradiated with γ-rays for 7 days

(10 Mrad) at room temperature. Gaseous components (26.5 g) were recovered to leave a colourless liquid identified as 4,4-dimethyl-1,1,1,2,3,3-hexafluoropentane **6** (8.8 g, 42%) bp 103–104 °C (Found: C, 40.1; H, 4.5. $C_7H_{10}F_6$ requires C, 40.4; H, 4.8%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.13 (9 H, s, CH_3), 4.91 (1 H, ddq, $^2J_{HF}$ 44, $^3J_{HF}$ 20, $^3J_{HF}$ 5.9, CFH); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −74.6 (3 F, m, CF_3), −117.6 and −126.1 (2 F, AB, J_{AB} 270, CF_2), −206.9 (1 F, dm, $^2J_{HF}$ 40, CFH); *m*/*z* (EI^+) 173 (5%), 65 (78), 57 (100), 41 (67).

2-Methylpropane (peroxide). 2-Methylpropane **5** (2.5 g, 43 mmol), HFP (8.2 g, 55 mmol) and DTBP (0.6 g, 4 mmol) were contained in a rocking autoclave at 140 °C for 24 h. Gaseous products (3.4 g) were recovered to leave a pale yellow liquid which on fractional distillation gave an isomeric mixture of 4,4-dimethyl-1,1,1,2,3,3-hexafluoropentane **6** (7.1 g, 80%) and 1,1,1,2,3,3-hexafluoro-5-methylhexane **7** (0.3 g, 3%) bp 103–104 °C (Found: C, 40.5; H, 4.9. $C_7H_{10}F_6$ requires C, 40.4; H, 4.8%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 0.88 (6 H, d, $^3J_{HH}$ 4.5, CH_3), 1.39 (1 H, br s, CH), 1.61 (2 H, m, CH_2), 4.91 (1 H, dm, $^2J_{HF}$ 44, CFH); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −75.5 (3 F, br s, CF_3), −105.9 and −109.5 (2 F, AB, J_{AB} 265, CF_2), −210.3 (1 F, br s, CFH); *m*/*z* (EI^+) 173 (6%), 47 (33), 43 (100), 41 (25).

***n*-Butane (γ-rays).** *n*-Butane **8** (5.8 g, 0.1 mol) and HFP (30.0 g, 0.2 mol) were irradiated with γ-rays for 5 days (7.5 Mrad) at room temperature. Gaseous components (29.8 g) were recovered to leave a liquid (5.4 g) which was separated by preparative scale GC into 4-methyl-1,1,1,2,3,3-hexafluorohexane **9** (6%, calculated by GC) (Found: C, 40.1; H, 4.4. $C_7H_{10}F_6$ requires C, 40.4; H, 4.8%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 0.97 (3 H, m, CH_3), 1.12 (3 H, m, CH_3), 1.30 (1 H, m, CH_2), 1.73 (1 H, m, CH_2), 2.06 (1 H, m, $CHCF_2$), 4.84 (1 H, dm, $^2J_{HF}$ 44, CFH); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −74.6 (3 F, m, CF_3), −116.4 and −119.3 (2 F, AB, J_{AB} 266, CF_2), −211.8 (1 F, d, $^2J_{HF}$ 44, CFH); *m*/*z* (EI^+) 160 (4%), 65 (18), 59 (17), 57 (100); and 4-methyl-1,1,1,2,3,3,7,7,8,9,9,9-dodecafluorononane **10** (11%, calculated by GC) (Found: C, 33.6; H, 2.5. $C_{10}H_{10}F_{12}$ requires C, 33.5; H, 2.8%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.08 (3 H, m, CH_3), 1.5–2.0 (5 H, m, CH_2 and $CHCF_2$), 4.76 (2 H, m, CFH); δ_C (100 MHz; $CDCl_3$; Me_4Si) 11.3 (br s, 4-Me), 22.7 (s, C-5), 32.9 (s, C-6), 36.7 (br s, C-4), 84.2 (m, CFH), 118.6 (m, CF_2), 134.6 (m, CF_3); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −74.7 (3 F, m, CF_3), −75.0 (3 F, m, CF_3), −107.7 and −111.9 (2 F, AB, J_{AB} 269, CF_2), −115.8 and −120.3 (2 F, AB, J_{AB} 271, CF_2), −210.6 (1 F, br s, CFH), −211.7 (1 F, d, $^2J_{HF}$ 45, CFH); *m*/*z* (EI^+) 319 (2%), 187 (57), 77 (53), 65 (98), 61 (100).

***n*-Hexane (peroxide).** *n*-Hexane **11** (8.6 g, 0.1 mol), HFP (30.0 g, 0.2 mol) and DTBP (0.6 g, 4 mmol) were contained in a rocking autoclave at 140 °C for 24 h. Gaseous products (23.3 g) were recovered to leave a liquid (6.5 g) which was separated by preparative scale GC into isomers of (1,1,2,3,3,3-hexafluoropropyl)-*n*-hexane **12** (1% by GC), δ_H (250 MHz; $CDCl_3$; Me_4Si) 0.9–1.9 (13 H, m, CH_3, CH_2 and $CHCF_2$), 4.47 (1 H, m, CFH); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −74.7 (3 F, m, CF_3), −111.3 (2 F, m, CF_2), −211.0 (1 F, br s, CFH); *m*/*z* (EI^+) 187 (1%), 151 (3), 85 (80), 57 (100); bis(1,1,2,3,3,3-hexafluoropropyl)-*n*-hexane **13** (8% by GC), δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.1–2.2 (12 H, m, CH_3, CH_2 and $CHCF_2$), 4.83 (2 H, m, CFH); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −74.8 (3 F, m, CF_3), −117.3 (2 F, m, CF_2), −211.0 (1 F, br s, CFH); *m*/*z* (EI^+) 265 (4%), 235 (59), 195 (46), 155 (51), 61 (100); tris(1,1,2,3,3,3-hexafluoropropyl)-*n*-hexane **14** (5% by GC); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.2–2.2 (11 H, m, CH_3, CH_2 and $CHCF_2$), 4.90 (3 H, m, CFH); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −75.2 (3 F, m, CF_3), −113.9 (2 F, m, CF_2), −211.0 (1 F, br s, CFH); *m*/*z* (EI^+) 477 (6%), 385 (40), 345 (64), 173 (68), 159 (72), 77 (90), 65 (100).

Cyclopentane (γ-rays). Cyclopentane **15** (7.1 g, 0.1 mol) and HFP (23.6 g, 0.16 mol) were irradiated with γ-rays for 5 days (7.5 Mrad) at room temperature. HFP (15.4 g) was recovered and a colourless liquid obtained. Cyclopentane (3.2 g) was removed by distillation, further fractional distillation gave two fractions. The first fraction was identified as (1,1,2,3,3,3-hexafluoropropyl)cyclopentane **16** (10.3 g, 86%) bp 134–135 °C (Found: C, 43.5; H, 4.6. $C_8H_{10}F_6$ requires C, 43.6; H, 4.6%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.63 (8 H, m, CH_2), 2.52 (1 H, m, $CHCF_2$), 4.74 (1 H, ddq, $^2J_{HF}$ 44, $^3J_{HF}$ 21, $^3J_{HF}$ 6.2, CFH); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −74.8 (3 F, m, CF_3), −114.4 and −118.8 (2 F, AB, J_{AB} 266, CF_2), −211.5 (1 F, d, $^2J_{HF}$ 38, CFH); δ_C (100 MHz; $CDCl_3$; Me_4Si) 25.1 (br s, C-4), 25.6 (s, C-3), 25.8 (s, C-5), 26.1 (br s, C-2), 42.5 (t, $^2J_{CF}$ 22, C-1), 86.0 (ddqd, $^1J_{CF}$ 195, $^2J_{CF}$ 37, $^2J_{CF}$ 34, $^2J_{CF}$ 30, CFH), 120.2 (ddd, $^1J_{CF}$ 251, $^1J_{CF}$ 249, $^2J_{CF}$ 24, CF_2), 120.9 (qd, $^1J_{CF}$ 282, $^2J_{CF}$ 26, CF_3); *m*/*z* (EI^+) 199 (2%), 69 (100), 42 (78), 41 (83), 39 (47); and the second fraction was identified as an isomeric mixture of 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclopentane (x = 2, 3) **17** bp[15] 80–81 °C (1.9 g, 9%) (Found: C, 36.0; H, 2.9. $C_{11}H_{10}F_{12}$ requires C, 35.7; H, 2.7%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.97 (6 H, m, CH_2), 2.64 (2 H, m, $CHCF_2$), 4.78 (2 H, m, CHF); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −74.9 (6 F, m, CF_3), −116.6 (4 F, m, CF_2), −211.2 (2 F, m, CFH); *m*/*z* (EI^+) 331 (19%), 219 (36), 199 (100), 77 (96), 69 (70).

Cyclopentane (peroxide). Cyclopentane **15** (7.0 g, 0.1 mol), HFP (29.5 g, 0.2 mol) and DTBP (0.6 g, 4 mmol) were contained in a rocking autoclave at 140 °C for 24 h. HFP (15.0 g) was recovered and a pale brown liquid obtained. Fractional distillation gave two fractions. The first fraction was identified as (1,1,2,3,3,3-hexafluoropropyl)cyclopentane **16** (12.5 g, 57%) and the second fraction was identified as 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclopentane (x = 2, 3) **17** (8.3 g, 23%).

Cyclohexane (γ-rays). Cyclohexane **18** (8.4 g, 0.1 mol) and hexafluoropropene (HFP) (22.9 g, 0.15 mol) were irradiated with γ-rays for 5 days (7.5 Mrad). HFP (10.9 g) was recovered and a colourless liquid obtained. Cyclohexane (1.8 g) was removed by distillation, further fractional distillation gave two fractions. The first fraction was identified as (1,1,2,3,3,3-hexafluoropropyl)cyclohexane **19** (16.6 g, 90%); bp 154–155 °C (Found: C, 46.4; H, 5.5. $C_9H_{12}F_6$ requires C, 46.2; H, 5.2%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.24 (5 H, m, CH_2), 1.84 (6 H, m, CH_2 and $CHCF_2$), 4.83 (1 H, ddqd, $^2J_{HF}$ 41, $^3J_{HF}$ 14, $^3J_{HF}$ 7.0, $^3J_{HF}$ 6.6, CHF); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −74.8 (3 F, m, CF_3), −114.4 and −118.8 (2 F, AB, J_{AB} 266, CF_2), −212.3 (1 F, d, $^2J_{HF}$ 41, CFH); δ_C (100 MHz; $CDCl_3$; Me_4Si) 24.0 (t, $^3J_{CF}$ 4.5, C-6), 25.3 (s, C-4), 25.5 (s, C-5), 25.6 (s, C-2), 25.8 (s, C-3), 41.6 (t, $^2J_{CF}$ 21, C-1), 84.8 (ddq, $^1J_{CF}$ 195, $^2J_{CF}$ 37, $^2J_{CF}$ 34, CFH), 119.9 (ddd, $^1J_{CF}$ 252, $^1J_{CF}$ 248, $^2J_{CF}$ 24, CF_2), 121.2 (qd, $^1J_{CF}$ 282, $^2J_{CF}$ 26, CF_3); *m*/*z* (EI^+) 234 (M^+, 1%), 195 (11), 83 (100), 55 (76); by comparison with data in the literature[10] the second fraction was identified as an isomeric mixture of 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (x = 2–4) **20** (1.2 g, 4%) bp[15] 105–106 °C (Found: C, 37.6; H, 3.3. $C_{12}H_{12}F_{12}$ requires C, 37.5; H, 3.1%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.33 (4 H, m, CH_2), 1.69 (6 H, m, CH_2), 2.09 (4 H, m, CH_2), 4.84 (2 H, dm, $^2J_{HF}$ 41, CHF); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −77.0 (6 F, m, CF_3), −120.9 (4 F, m, CF_2), −213.8 (1 F, m, CFH), −214.6 (1 F, m, CFH); *m*/*z* (EI^+) 345 (12%), 233 (100), 213 (77), 77 (47).

Cyclohexane (peroxide). Cyclohexane **18** (8.3 g, 0.1 mol), HFP (30.0 g, 0.2 mol) and DTBP (0.6 g, 4 mmol) were contained in a rocking autoclave at 140 °C for 24 h. HFP (7.4 g) was recovered and a yellow liquid obtained. Cyclohexane (0.1 g) was removed by distillation, further fractional distillation of the liquid gave two fractions. The first fraction was identified as (1,1,2,3,3,3-hexafluoropropyl)cyclohexane **19** (9.0 g, 39%), and

the second fraction was identified as mixture of isomers of 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (x = 2–4) **20** (20.1 g, 53%), from which 2*R*,2′*S*-*trans*-1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane **20a** (3.4 g, 9%) crystallised out on standing as a white solid; mp 80–81 °C (from MeOH) (Found: C, 37.3; H, 3.0. $C_{12}H_{12}F_{12}$ requires C, 37.5; H, 3.1%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.36 (4 H, m, CH_2), 2.07 (6 H, m, CH_2 + CH), 4.83 (2 H, ddq, $^2J_{HF}$ 44, $^3J_{HF}$ 21, $^3J_{HF}$ 6.0, CFH); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −74.2 (3 F, m, CF_3), −117.1 and −118.4 (2 F, AB, J_{AB} 268, CF_2), −211.2 (1 F, d, $^2J_{HF}$ 44, CFH); δ_C (100 MHz; $CDCl_3$; Me_4Si) 22.8 (t, $^3J_{CF}$ 4.4, C-3), 24.1 (t, $^3J_{CF}$ 2.9, C-2), 40.6 (t, $^2J_{CF}$ 22, C-1), 85.0 (ddqd, $^1J_{CF}$ 196, $^2J_{CF}$ 38, $^2J_{CF}$ 34, $^2J_{CF}$ 31, CFH), 119.3 (ddd, $^1J_{CF}$ 253, $^1J_{CF}$ 249, $^2J_{CF}$ 24, CF_2), 121.2 (qd, $^1J_{CF}$ 282, $^2J_{CF}$ 26, CF_3); *m*/*z* (EI^+) 345 (12%), 233 (100), 213 (87).

***trans*-Decahydronaphthalene (γ-rays).** *trans*-Decahydronaphthalene **21** (6.9 g, 0.05 mol), HFP (15.5 g, 0.1 mol) and dry acetone (8 ml) were irradiated with γ-rays at room temperature for 5 days (7.5 Mrad). Nearly all of the HFP (14.7 g) was recovered. The liquid product mixture (7.5 g) was analysed by GC/MS and ^{19}F NMR which identified traces of x-(1,1,2,3,3,3-hexafluoropropyl)-*trans*-decahydronaphthalene (x = 1, 2) **22** (*ca.* 5% by GC) and no further workup was performed.

***trans*-Decahydronaphthalene (peroxide).** *trans*-Decahydronaphthalene **21** (13.9 g, 0.1 mol), HFP (23.1 g, 0.15 mol), DTBP (0.8 g, 5.5 mmol) and dry acetone (2 ml) were contained in a rocking autoclave at 140 °C for 24 hours. HFP (4.1 g) was recovered and a yellow liquid (33.3 g) obtained. Acetone and *trans*-decahydronaphthalene (2.9 g) were removed by distillation, further fractional distillation of the liquid under reduced pressure gave two fractions. The first fraction was identified as an isomeric mixture of x-(1,1,2,3,3,3-hexafluoropropyl)-*trans*-decahydronaphthalene (x = 1, 2) **22** (11.5 g, 51%), bp[5] 80–82 °C (Found: C, 54.2; H, 6.1. $C_{13}H_{18}F_6$ requires C, 54.2; H, 6.3%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.00 to 1.69 (16 H, overlapping m, CH + CH_2), 2.10 (1 H, overlapping m, $CHCF_2$), 4.82 (1 H, m, CHF); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −74.0, −74.5 (3 F, br s, CF_3), −110.2, −118.6 (2 F, overlapping m, CF_2), −211.1, 211.9 (1 F, m, CFH); *m*/*z* (EI^+) 288 (M^+, 57%), 246 (43), 137 (37), 95 (100), 81 (81), 67 (75), 41 (80); and the second fraction was identified as an isomeric mixture of x,y-bis(1,1,2,3,3,3-hexafluoropropyl)-*trans*-decahydronaphthalene (x = 1, y = 2–10; x = 2, y = 3–10) **23** (9.5 g, 27%), bp[5] 130–135 °C (Found: C, 43.6; H, 4.0. $C_{16}H_{18}F_{12}$ requires C, 43.8; H, 4.1%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.00 to 1.70 (14 H, overlapping m, CH + CH_2), 2.10 (2 H, overlapping m, $CHCF_2$), 4.83 (2 H, m, CHF); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −73.8, −74.2 (6 F, br s, CF_3), −118.0 (4 F, overlapping m, CF_2), −211.1 (2 F, overlapping m, CFH); *m*/*z* (EI^+) 438 (M^+, 7%), 287 (60), 246 (89), 231 (84), 81 (100).

***cis*-Decahydronaphthalene (γ-rays).** *cis*-Decahydronaphthalene **21** (6.9 g, 0.05 mol), HFP (15.3 g, 0.1 mol) and dry acetone (8 ml) were irradiated with γ-rays at room temperature for 5 days (7.5 Mrad). Nearly all of the HFP (14.5 g) was recovered. The colourless liquid product mixture (7.6 g) was analysed by GC/MS and ^{19}F NMR which identified traces of x-(1,1,2,3,3,3-hexafluoropropyl)-*cis*-decahydronaphthalene (x = 1, 2, 9) **22** (*ca.* 5% by GC), but no further workup was performed.

***cis*-Decahydronaphthalene (peroxide).** *cis*-Decahydronaphthalene **24** (13.8 g, 0.1 mol), HFP (29.1 g, 0.2 mol), DTBP (0.6 g, 4 mmol) and dry acetone (2 ml) were contained in a rocking autoclave at 140 °C for 24 hours. HFP (19.8 g) was recovered and a yellow liquid (23.3 g) obtained. Acetone and *cis*-decahydronaphthalene (8.4 g) were removed by distillation, further fractional distillation of the liquid under reduced pressure gave two fractions. The first fraction was identified as an isomeric mixture of x-(1,1,2,3,3,3-hexafluoropropyl)-*cis*-decahydronaphthalene (x = 1, 2, 9) **25** (6.3 g, 56%) bp[20] 120–121 °C (Found: C, 54.2; H, 6.1. $C_{13}H_{18}F_6$ requires C, 54.2; H, 6.3%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.31 to 1.70 (16 H, overlapping m, CH + CH_2), 2.08 to 2.20 (1 H, m, $CHCF_2$), 4.80 (1 H, m, CHF); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −74.5, −74.8 (3 F, br s, CF_3), −111.4 to −118.5 (2 F, overlapping m, CF_2), −206.4, −212.1 (1 F, m, CFH); *m*/*z* (EI^+) 288 (M^+, 64%), 246 (64), 137 (47), 95 (100); and the second fraction was identified as an isomeric mixture of x,y-bis(1,1,2,3,3,3-hexafluoropropyl)-decalin (x = 1, y = 2–10; x = 2, y = 3–10) **26** (5.6 g, 33%), bp[20] 152–153 °C (Found: C, 43.6; H, 4.0. $C_{16}H_{18}F_{12}$ requires C, 43.8; H, 4.1%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.39 to 2.05 (14 H, overlapping m, CH + CH_2), 2.23 to 2.65 (2 H, overlapping m, $CHCF_2$), 4.80, 4.98 (2 H, overlapping m, CHF); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −74.2, −74.6 (6 F, br s, CF_3), −111.4 to −119.4 (4 F, overlapping m, CF_2), −204.1, −206.2, −212.1 (2 F, m, CFH); *m*/*z* (EI^+) 400 (1%), 287 (72), 245 (100), 231 (88).

Bicyclo[2.2.1]heptane (γ-rays). Bicyclo[2.2.1]heptane **27** (7.2 g, 75 mmol), HFP (15.7 g, 0.1 mol) and dry acetone (8 ml) were irradiated with γ-rays at room temperature for 5 days (7.5 Mrad). HFP (5.5 g) was recovered and a colourless liquid obtained. Sublimation gave recovered bicyclo[2.2.1]heptane (2.5 g), and subsequent fractional distillation under reduced pressure gave two fractions. The first fraction was identified as two diastereomers of *exo*-2-(1,1,2,3,3,3-hexafluoropropyl)-bicyclo[2.2.1]heptane **28** (9.6 g, 80%) bp[20] 80 °C (Found: C, 48.8; H, 4.8. $C_{10}H_{12}F_6$ requires C, 48.8; H, 4.9%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.26 (3 H, overlapping m, CH_2), 1.61 (4 H, overlapping m, CH_2), 1.75 (1 H, m, CH_2), 2.14 (1 H, m, $CHCF_2$), 2.37 (1 H, br s, CH), 2.45 (1 H, br s, CH), 4.81 (1 H, m, CHF); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −74.7 (3 F, br s, CF_3), −113.0 and −118.8 (2 F, AB, J_{AB} 265, CF_2), −211.2 (1 F, d, $^2J_{HF}$ 44, CFH); δ_C (100 MHz; $CDCl_3$; Me_4Si) 28.0 (br s, C-6), 30.4 (s, C-5), 31.4 (s, C-3), 35.8 (s, C-4), 36.9 (br s, C-7), 37.6 (d, $^4J_{CF}$ 5, C-1), 44.9 (t, $^2J_{CF}$ 22, C-2), 86.2 (ddqd, $^1J_{CF}$ 196, $^2J_{CF}$ 37, $^2J_{CF}$ 34, $^2J_{CF}$ 31, CFH), 120.0 (ddd, $^1J_{CF}$ 251, $^1J_{CF}$ 249, $^2J_{CF}$ 22, CF_2), 121.3 (qd, $^1J_{CF}$ 282, $^2J_{CF}$ 29, CF_3); *m*/*z* (EI^+) 246 (M^+, 5%), 95 (57), 68 (87), 67 (100); and the second fraction was identified as an isomeric mixture of 2,x-bis(1,1,2,3,3,3-hexafluoropropyl)-bicyclo[2.2.1]heptane (x = 5, 6) **29** (2.3 g, 12%) bp[20] 120 °C (Found: C, 39.4; H, 3.0. $C_{13}H_{12}F_{12}$ requires C, 39.4; H, 3.1%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.00 (3 H, overlapping m, CH_2), 1.50 (5 H, overlapping m, CH_2), 2.15 (1 H, m, $CHCF_2$), 2.32, 2.39 (1 H, br s, CH), 2.54, 2.80 (1 H, br s, CH), 4.75 (1 H, m, CHF); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −74.7 (6 F, overlapping m, CF_3), −114.1 (4 F, overlapping m, CF_3), −210.8 (2 F, overlapping m, CFH); *m*/*z* (EI^+) 245 (9%), 77 (22), 67 (100), 41 (14).

Bicyclo[2.2.1]heptane (peroxide). Bicyclo[2.2.1]heptane **27** (6.1 g, 64 mmol), HFP (14.3 g, 90 mmol) and DTBP (0.6 g, 4 mmol) were contained in a rocking autoclave for 24 hours at 140 °C. No HFP was recovered and a pale yellow liquid (19.5 g) was obtained. Fractional distillation of the liquid gave two fractions, the first consisted of *exo*-2-(1,1,2,3,3,3-hexafluoropropyl)-bicyclo[2.2.1]heptane **28** (7.1 g, 45%) and the second consisted of 2,x-bis(1,1,2,3,3,3-hexafluoropropyl)bicyclo[2.2.1]heptane (x = 5, 6) **29** (9.5 g, 37%).

Adamantane (peroxide). Adamantane **30** (13.8 g, 0.1 mol), HFP (17.6 g, 0.12 mol) and DTBP (0.7 g, 5 mmol) were contained in a rocking autoclave for 24 hours at 140 °C. No HFP was recovered and adamantane (1.1 g) crystallised out of the liquid product (28.0 g). Fractional distillation under reduced pressure gave two fractions, the first fraction was identified as 1-(1,1,2,3,3,3-hexafluoropropyl)adamantane **31** (16.3 g, 60%), bp[9] 99–101 °C (Found: C, 54.4; H, 5.5. $C_{13}H_{16}F_6$ requires C, 54.5; H, 5.6%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.76 (12 H, m, CH_2), 2.07 (3 H, s, CH), 4.93 (1 H, ddq, $^2J_{HF}$ 44, $^3J_{HF}$ 20, $^3J_{HF}$ 6.4, CFH); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −74.3 (3 F, br s, CF_3),

−122.6 and −130.0 (2 F, AB, J_{AB} 274, CF_2), −206.9 (1 F, d, $^2J_{HF}$ 41, CFH); δ_C (100 MHz; $CDCl_3$; Me_4Si) 27.5 (s, CH), 34.6 (q, $^5J_{CF}$ 3.4, CH_2), 36.4 (s, CH_2), 40.0 (t, $^2J_{CF}$ 21, CCF_2), 83.6 (ddqd, $^1J_{CF}$ 197, $^2J_{CF}$ 41, $^2J_{CF}$ 33, $^2J_{CF}$ 26, CFH), 119.5 (ddd, $^1J_{CF}$ 261, $^1J_{CF}$ 247, $^2J_{CF}$ 22, CF_2), 121.3 (qd, $^1J_{CF}$ 283, $^2J_{CF}$ 26, CF_3); *m/z* (EI^+) 151 (1%), 135 (100), 79 (43), 41 (35); MS and NMR data are consistent with those contained in the literature;[8] and the second fraction was identified as 1,3-bis-(1,1,2,3,3,3-hexafluoropropyl)adamantane **32** (7.9 g, 19%), bp[9] 124–126 °C (Found: C, 43.7; H, 3.8. $C_{16}H_{16}F_{12}$ requires C, 44.0; H, 3.7%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.80 (12 H, m, CH + CH_2), 2.28 (2 H, br s, CH_2), 4.93 (2 H, ddq, $^2J_{HF}$ 44, $^3J_{HF}$ 20, $^3J_{HF}$ 6.4, CFH); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −74.3 (6 F, br s, CF_3), −121.7 and −129.4 (4 F, AB, J_{AB} 275, CF_2), −207.1 (2 F, d, $^2J_{HF}$ 37, CFH); δ_C (100 MHz; $CDCl_3$; Me_4Si) 27.0 (s, CH), 31.8 (br s, CH_2), 33.8 (s, CH_2), 35.3 (s, CH_2), 40.6 (t, $^2J_{CF}$ 21, CCF_2), 83.8 (ddqd, $^1J_{CF}$ 197, $^2J_{CF}$ 42, $^2J_{CF}$ 34, $^2J_{CF}$ 26, CFH), 119.1 (ddd, $^1J_{CF}$ 261, $^1J_{CF}$ 247, $^2J_{CF}$ 23, CF_2), 121.1 (qd, $^1J_{CF}$ 283, $^2J_{CF}$ 26, CF_3); *m/z* (EI^+) 397 (1%), 285 (100), 243 (11), 229 (12), 55 (16); MS and NMR data are consistent with those contained in the literature.[21]

Adamantane (peroxide). Adamantane **30** (2.7 g, 20 mmol), HFP (20.8 g, 140 mmol) and DTBP (0.5 g, 4 mmol) were contained in a rocking autoclave for 24 hours at 140 °C. HFP (8.9 g) was recovered and a waxy liquid (12.7 g) obtained. Kugelrohr distillation (175 °C, 1 mmHg) gave a waxy mixture which was then mixed with chloroform, at which point a white solid precipitated out. Filtration of the solid, followed by removal of the solvent gave a liquid identified as 1,3,5-tris(1,1,2,3,3,3-hexafluoropropyl)adamantane **33** (6.9 g, 59%), bp[9] 143–145 °C (Found: C, 39.1; H, 2.5. $C_{19}H_{16}F_{18}$ requires C, 38.9; H, 2.7%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.83 (12 H, m, CH_2), 2.15 (1 H, br s, CH), 4.95 (2 H, ddq, $^2J_{HF}$ 41, $^3J_{HF}$ 19, $^3J_{HF}$ 5.3, CFH); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −74.2 (9 F, br s, CF_3), −120.7 and −128.7 (6 F, AB, J_{AB} 274, CF_2), −207.3 (3 F, d, $^2J_{HF}$ 29, CFH); δ_C (100 MHz; $CDCl_3$; Me_4Si) 26.7 (s, CH), 31.5 (s, CH_2), 33.2 (s, CH_2), 41.3 (t, $^2J_{CF}$ 22, CCF_2), 84.1 (ddqd, $^1J_{CF}$ 197, $^2J_{CF}$ 42, $^2J_{CF}$ 34, $^2J_{CF}$ 26, CFH), 119.1 (ddd, $^1J_{CF}$ 262, $^1J_{CF}$ 248, $^2J_{CF}$ 26, CF_2), 121.0 (qd, $^1J_{CF}$ 283, $^2J_{CF}$ 26, CF_3); *m/z* (EI^+) 547 (5%), 435 (100), 277 (15), 243 (12), 69 (34); MS and NMR data are consistent with those contained in the literature;[18] and the white solid was identified as 1,3,5,7-tetrakis(1,1,2,3,3,3-hexafluoropropyl)-adamantane **34** (5.3 g, 36%) mp 110–112 °C (from MeOH) (Found: C, 36.0; H, 2.2. $C_{22}H_{16}F_{24}$ requires C, 35.9; H, 2.2%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 2.07 (12 H, m, CH_2), 5.99 (4 H, ddq, $^2J_{HF}$ 42, $^3J_{HF}$ 20, $^3J_{HF}$ 6.4, CFH); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −74.1 (12 F, br s, CF_3), −121.1 and −127.6 (8 F, AB, J_{AB} 276, CF_2), −207.1 (4 F, d, $^2J_{HF}$ 29, CFH); δ_C (100 MHz; $CDCl_3$; Me_4Si) 30.1 (s, CH_2), 41.6 (t, $^2J_{CF}$ 22, CCF_2), 83.1 (ddq, $^1J_{CF}$ 194, $^2J_{CF}$ 39, $^2J_{CF}$ 34, CFH), 119.0 (ddd, $^1J_{CF}$ 261, $^1J_{CF}$ 249, $^2J_{CF}$ 22, CF_2), 121.4 (qd, $^1J_{CF}$ 282, $^2J_{CF}$ 26, CF_3); *m/z* (EI^+) 717 (1%), 697 (4), 585 (100), 277 (33), 151 (55), 55 (65).

General procedure for competition reactions

Competition reactions were performed using either DTBP or γ-ray initiation using the usual experimental procedure described previously. A 0.15 molar deficiency of HFP to hydrocarbon was used. The reactions were followed by the disappearance of hydrocarbons from capillary GC traces (Flame ionisation detector) before and after the reaction, therefore eliminating any differences in detector responses.

Competition between cyclohexane and *n*-hexane. A Carius tube was charged with cyclohexane **18** (8.4 g, 0.1 mol), *n*-hexane **11** (8.6 g, 50 mmol) and HFP (4.6 g, 30 mmol) and then irradiated with γ-rays for 10 days. The Carius tube was opened and any remaining HFP recovered. The GC traces from before and after the reaction showed the peak integration of cyclohexane decreased from 48.56% to 11.7% and the peak integration of *n*-hexane decreased from 48.42% to 10.5%.

Competition between cyclopentane and *n*-hexane. A Carius tube was charged with cyclopentane **15** (7.0 g, 0.1 mol), *n*-hexane **11** (8.6 g, 50 mmol) and HFP (4.6 g, 30 mmol) and then irradiated with γ-rays for 10 days. The Carius tube was opened and any remaining HFP recovered. The GC traces from before and after the reaction showed the peak integration of cyclopentane decreased from 44.60% to 38.81% and the peak integration of *n*-hexane decreased from 47.07% to 38.50%.

Competition between *cis*- and *trans*-decahydronaphthalene. An autoclave (150 ml) was charged with *cis*-decahydronaphthalene **24** (6.9 g, 50 mmol), *trans*-decahydronaphthalene **21** (6.9 g, 50 mmol), HFP (2.3 g, 15 mmol) and DTBP (0.3 g, 2 mmol) and then rocked at 140 °C for 24 h. The autoclave was opened and HFP (0.1 g) was recovered. The GC traces from before and after the reaction showed the peak integration of *cis*-decahydronaphthalene decreased from 52.18% to 43.12% and the peak integration of *trans*-decahydronaphthalene decreased from 47.82% to 43.69%.

Competition between cyclohexane and *trans*-decahydronaphthalene. An autoclave (150 ml) was charged with cyclohexane **18** (4.2 g, 50 mmol), *trans*-decahydronaphthalene **21** (6.9 g, 50 mmol), HFP (2.4 g, 16 mmol) and DTBP (0.3 g, 2 mmol) and then rocked at 140 °C for 24 h. No HFP was recovered and the GC traces showed the peak integration of cyclohexane decreased from 53.41% to 49.75% and the peak integration of *trans*-decahydronaphthalene decreased from 46.58% to 34.46%.

Competition between cyclohexane and cyclopentane. An autoclave (150 ml) was charged with cyclohexane **18** (4.2 g, 50 mmol), cyclopentane **15** (3.5 g, 50 mmol), HFP (2.4 g, 16 mmol) and DTBP (0.3 g, 2 mmol) and then rocked at 140 °C for 24 h. No HFP was recovered. The GC traces showed the peak integration of cyclohexane decreased from 54.76% to 44.54% and the peak integration of cyclopentane decreased from 45.13% to 36.94%.

Competition between cyclohexane and tetrahydropyran. A Carius tube was charged with cyclohexane **18** (8.4 g, 0.1 mol), tetrahydropyran **35** (8.6 g, 50 mmol) and HFP (4.6 g, 30 mmol) and then irradiated with γ-rays for 10 days. The Carius tube was opened and any remaining HFP recovered. The GC traces from before and after the reaction showed the peak integration of cyclohexane decreased from 58.92% to 44.38% and the peak integration of tetrahydropyran decreased from 41.08% to 29.50%.

Competition between (1,1,2,3,3,3-hexafluoropropyl)tetrahydrofuran and tetrahydrofuran. A Carius tube was charged with (1,1,2,3,3,3-hexafluoropropyl)tetrahydrofuran **36** (11.1 g, 50 mmol), tetrahydrofuran **37** (3.6 g, 50 mmol) and HFP (2.3 g, 15 mmol) and then irradiated with γ-rays for 10 days. The Carius tube was opened and any remaining HFP recovered. The GC traces from before and after the reaction showed the peak integration of (1,1,2,3,3,3-hexafluoropropyl)tetrahydrofuran increased from 67.51% to 76.51% whilst the peak integration of tetrahydropyran decreased from 31.49% to 22.56%.

General procedure for elimination of hydrogen fluoride from hexafluoropropene adducts

The hexafluoropropene adduct was added dropwise to a stirred solution/suspension of the alkoxide in its solvent. The reaction was monitored by the ^{19}F NMR spectra of the reaction mixture

and when elimination was complete the mixture was poured into water, neutralised with 10% HCl, the organic layer was separated and dried over $MgSO_4$ and the products purified by distillation.

Eliminations from:

(1,1,2,3,3,3-Hexafluoropropyl)cyclopentane. Addition of (1,1,2,3,3,3-hexafluoropropyl)cyclopentane **16** (4.4 g, 20 mmol) to sodium *tert*-butoxide (5.0 g, 40 mmol) in diethyl ether (40 ml) at −78 °C for 30 minutes gave (1*Z*)-pentafluoroprop-1-enylcyclopentane **38** (3.0 g, 75%) bp 119–121 °C (Found: C, 47.9; H, 4.5. $C_8H_9F_5$ requires C, 48.0; H, 4.5%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.63 (9 H, m, ring H), 2.52 (1 H, dm, $^3J_{HF}$ 32, CHCF); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −66.2 (3 F, br s, CF_3), −133.9 (1 F, d, $^3J_{HF}$ 32, CHCF), −160.1 (1 F, br s, $CFCF_3$); δ_C (100 MHz; $CDCl_3$; Me_4Si) 26.2 (s, C-3), 29.5 (s, C-2), 36.8 (d, $^2J_{CF}$ 22, C-1), 120.4 (qdd, $^1J_{CF}$ 270, $^2J_{CF}$ 35, $^3J_{CF}$ 9.6, CF_3), 134.7 (dqd, $^1J_{CF}$ 250, $^2J_{CF}$ 40, $^2J_{CF}$ 24, *C*FCF$_3$), 155.3 (ddq, $^1J_{CF}$ 264, $^2J_{CF}$ 10, $^3J_{CF}$ 3.5, CH*C*F); *m*/*z* (EI$^+$) 200 (M^+, 13%), 158 (60), 68 (98), 42 (100), 41 (89), 39 (82).

1,x-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclopentane (x = 2, 3). Addition of 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclopentane **17** (7.4 g, 20 mmol) to sodium *tert*-butoxide (9.0 g, 80 mmol) in diethyl ether (50 ml) at −78 °C for 30 minutes gave an isomeric mixture of 1,x-bis[(1*Z*)-pentafluoroprop-1-enyl]cyclopentane (x = 2, 3) **39** (4.0 g, 60%) bp[21] 76–77 °C (Found: C, 43.9; H, 2.6. $C_{11}H_8F_{10}$ requires C, 43.7; H, 2.4%) including 1,3-bis[(1*Z*)-pentafluoroprop-1-enyl]cyclopentane **39a** δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.65 (6 H, m, CH_2), 2.50 (2 H, m, CHCF); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −66.9 (6 F, br s, CF_3), −135.0 (2 F, br s, CHCF), −159.3 (2 F, br s, $CFCF_3$); δ_C (100 MHz; $CDCl_3$; Me_4Si) 29.9 (s, C4/5), 31.4 (s, C-2), 36.6 (dm, $^2J_{CF}$ 22, C-1/3), 120.0 (qdd, $^1J_{CF}$ 270, $^2J_{CF}$ 35, $^3J_{CF}$ 9.6, CF_3), 135.2 (dqd, $^1J_{CF}$ 252, $^2J_{CF}$ 40, $^2J_{CF}$ 24, *C*FCF$_3$), 153.6 (ddq, $^1J_{CF}$ 264, $^2J_{CF}$ 11, $^3J_{CF}$ 3.4, CH*C*F); *m*/*z* (EI$^+$) 330 (M^+, 13%), 197 (100), 158 (65), 51 (62); and 1,2-bis[(1*Z*)-pentafluoroprop-1-enyl]cyclopentane **39b** δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.65 (6 H, m, CH_2), 2.50 (2 H, m, CHCF); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −66.9 (6 F, br s, CF_3), −135.9 (1 F, d, $^3J_{HF}$ 31, CHCF), −156.4 (1 F, s, $CFCF_3$); δ_C (100 MHz; $CDCl_3$; Me_4Si) 25.1 (s, C-4), 28.9 (s, C-3/5), 40.3 (dm, $^2J_{CF}$ 23, C-1/2), 119.8 (qm, $^1J_{CF}$ 270, CF_3), 136.5 (d, $^1J_{CF}$ 250, *C*FCF$_3$), 151.4 (dm, $^1J_{CF}$ 268, CH*C*F); *m*/*z* (EI$^+$) 330 (M^+, 1%), 158 (100), 103 (40), 69 (54).

(1,1,2,3,3,3-Hexafluoropropyl)cyclohexane. Addition of (1,1,2,3,3,3-hexafluoropropyl)cyclohexane **19** (70.2 g, 0.3 mol) to sodium *tert*-butoxide (50.5 g, 0.45 mol) in dry diisopropyl ether (100 ml) at 0 °C for 30 min gave (1*Z*)-pentafluoroprop-1-enylcyclohexane **40** (59.1 g, 92%) bp 139–140 °C (Found: C, 50.6; H, 5.2. $C_9H_{11}F_5$ requires C, 50.5; H, 5.2%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.20 (1 H, qt, $^{2,3}J_{HH}$ 12, $^3J_{HH}$ 3.2, H-4), 1.31 (2 H, qm, $^{2,3}J_{HH}$ 12, H-3/5), 1.55 (2 H, qd, $^{2,3}J_{HH}$ 12, $^3J_{HH}$ 3.2, H-2/6), 1.72 (3 H, dm, $^3J_{HH}$ 12, H-2/4/6), 1.83 (2 H, d, $^4J_{HF}$ 12, H-3/5), 2.52 (1 H, dt, $^3J_{HF}$ 32, $^3J_{HH}$ 12, H-1); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −66.2 (3 F, br s, CF_3), −131.4 (1 F, d, $^3J_{HF}$ 32, CHCF), −161.7 (1 F, br s, $CFCF_3$); δ_C (100 MHz; $CDCl_3$; Me_4Si) 25.6 (s, C-4), 25.9 (s, C-3/5), 28.9 (d, $^3J_{CF}$ 2.2, C-2/6), 36.7 (d, $^2J_{CF}$ 21, C-1), 120.4 (qdd, $^1J_{CF}$ 270, $^2J_{CF}$ 35, $^3J_{CF}$ 9.6, CF_3), 134.9 (dqd, $^1J_{CF}$ 250, $^2J_{CF}$ 40, $^2J_{CF}$ 24, *C*FCF$_3$), 156.6 (ddq, $^1J_{CF}$ 264, $^2J_{CF}$ 9.6, $^3J_{CF}$ 3.4, CH*C*F); *m*/*z* (EI$^+$) 214 (M^+, 40%), 158 (91), 100 (88), 82 (79), 56 (77), 41 (100).

***trans*-1,4-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane.** Addition of *trans*-1,4-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane **20a** (3.5 g, 9 mmol) to sodium *tert*-butoxide (2.1 g, 18 mmol) in dry diisopropyl ether (25 ml) at −10 °C, using a salt–ice bath, for 30 min gave *trans*-1,4-bis[(1*Z*)-pentafluoroprop-1-enyl]-cyclohexane **41a** (2.1 g, 67%) mp 101–102 °C (from MeOH) (Found: C, 41.8; H, 2.9. $C_{12}H_{10}F_{10}$ requires C, 41.9; H, 2.9%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.69 (4 H, m, H-2/3/5/6), 1.89 (4 H, d, $^3J_{HH}$ 7.2, H-2/3/5/6), 2.56 (2 H, dm, $^3J_{HF}$ 32, H-1/4); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −65.9 (3 F, br s, CF_3), −132.2 (1 F, dm, $^3J_{HF}$ 32, CHCF), −159.2 (1 F, br s, $CFCF_3$); δ_C (100 MHz; $CDCl_3$; Me_4Si) 27.8 (s, C-2/3/4/5), 35.5 (d, $^3J_{CF}$ 21, C-1/4), 120.2 (qdd, $^1J_{CF}$ 270, $^2J_{CF}$ 35, $^3J_{CF}$ 9.6, CF_3), 135.3 (dqd, $^1J_{CF}$ 252, $^3J_{CF}$ 40, $^3J_{CF}$ 24, *C*FCF$_3$), 155.3 (dd, $^1J_{CF}$ 266, $^3J_{CF}$ 10, CH*C*F); *m*/*z* (EI$^+$) 344 (M^+, 9%), 158 (83), 108 (83), 95 (100), 54 (93).

1,x-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (x = 2–4). Addition of 1,x-bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane **20** (16.0 g, 40 mmol) in diethyl ether (30 ml) to sodium *tert*-butoxide (15.9 g, 0.14 mol) in diethyl ether (50 ml) at −10 °C for 30 minutes gave a fraction which was identified as a mixture of *cis*-1,3-bis[(1*Z*)-pentafluoroprop-1-enyl]cyclohexane **41b** (8.2 g, 57%) bp[20] 92–93 °C (Found: C, 41.7; H, 2.9. $C_{12}H_{10}F_{10}$ requires C, 41.9; H, 2.9%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.42 (1 H, qm, $^{2,3}J_{HH}$ 12, H-5), 1.57 (2 H, qd, $^{2,3}J_{HH}$ 12, $^3J_{HH}$ 3.6, H-4/6), 1.77 (3 H, m, H-4/5/6), 1.88 (1 H, q, $^{2,3}J_{HH}$ 13, H-2), 2.10 (1 H, d, $^2J_{HH}$ 13, H-2), 2.64 (2 H, dt, $^3J_{HF}$ 31, $^3J_{HH}$ 12, H-1/3); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −66.3 (3 F, br s, CF_3), −132.2 (1 F, d, $^3J_{HF}$ 31, CHCF), −159.1 (1 F, br s, $CFCF_3$); δ_C (100 MHz; $CDCl_3$; Me_4Si) 24.6 (s, C-5), 27.4 (d, $^3J_{CF}$ 2.3, C-4/6), 30.0 (s, C-2), 35.6 (d, $^2J_{CF}$ 21, C-1/3), 119.8 (qdd, $^1J_{CF}$ 270, $^2J_{CF}$ 35, $^3J_{CF}$ 9.6, CF_3), 135.1 (dqd, $^1J_{CF}$ 253, $^2J_{CF}$ 41, $^2J_{CF}$ 24, *C*FCF$_3$), 154.5 (ddq, $^1J_{CF}$ 266, $^2J_{CF}$ 11, $^3J_{CF}$ 3.5, CH*C*F); *m*/*z* (EI$^+$) 344 (M^+, 8%), 211 (45), 158 (94), 54 (100), 41 (85); and *trans*-1,4-bis[(1*Z*)-pentafluoroprop-1-enyl]cyclohexane **41a** (4.3 g, 30%) which precipitated out on cooling in an acetone–carbon dioxide bath (−78 °C).

x-(1,1,2,3,3,3-Hexafluoropropyl)-*trans*-decahydronaphthalene (x = 1, 2). x-(1,1,2,3,3,3-Hexafluoropropyl)-*trans*-decahydronaphthalene (x = 1, 2) **22** (5.8 g, 20 mmol) was added to sodium *tert*-butoxide (4.5 g, 40 mmol) in dry diethyl ether (20 ml), cooled to −10 °C, and stirred for 30 minutes. Fractional distillation gave an isomeric mixture of x-[(1*Z*)-pentafluoroprop-1-enyl]-*trans*-decahydronaphthalene (x = 1, 2) **42** (4.4 g, 82%) bp[6] 75–77 °C (Found: C, 58.1; H, 6.6. $C_{13}H_{17}F_5$ requires C, 58.2; H, 6.3%); 2-[(1*Z*)-pentafluoroprop-1-enyl]-*trans*-decahydronaphthalene **42b** δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.02 to 1.72 (16 H, overlapping m, CH + CH_2), 2.58 (1 H, dm, $^3J_{HF}$ 32, CHCF); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −66.3 (3 F, br s, CF_3), −131.7 (1 F, d, $^3J_{HF}$ 32, CHCF), −161.5 (1 F, br s, *C*FCF_3); δ_C (100 MHz; $CDCl_3$; Me_4Si) 26.4 (s, C-6), 26.5 (s, C-7), 28.5 (d, $^5J_{CF}$ 2.7, C-3), 32.8 (s, C-4), 33.5 (s, C-5), 33.6 (s, C-8), 35.6 (d, $^5J_{CF}$ 2.6, C-1), 36.4 (dm, $^2J_{CF}$ 21, C-2), 42.2 (s, C-10), 42.3 (s, C-9), 120.0 (qdd, $^1J_{CF}$ 271, $^2J_{CF}$ 35, $^3J_{CF}$ 9.6, CF_3), 135.5 (dqd, $^1J_{CF}$ 250, $^2J_{CF}$ 40, $^2J_{CF}$ 24, *C*FCF$_3$), 156.0 (ddq, $^1J_{CF}$ 266, $^2J_{CF}$ 9.4, $^3J_{CF}$ 3.4, CH*C*F); *m*/*z* (EI$^+$) 268 (M^+, 17%), 135 (71), 67 (65), 41 (100); 1-[(1*Z*)-1,2,3,3,3-pentafluoroprop-1-enyl]-*trans*-decahydronaphthalene **42a** δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.02 to 1.72, (16 H, overlapping m, CH + CH_2), 2.23 (1 H, dm, $^3J_{HF}$ 33, CHCF); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −65.7 (3 F, br s, CF_3), −133.1 (1 F, d, $^3J_{HF}$ 33, CHCF), −160.0 (1 F, br s, $CFCF_3$); δ_C (100 MHz; $CDCl_3$; Me_4Si) 25.3 (s, C-6), 26.2 (s, C-7), 26.3 (s, C-3), 29.5 (s, C-2), 30.1 (s, C-5), 33.3 (s, C-4), 33.5 (dm, $^2J_{CF}$ 21, C-1), 34.0 (s, C-8), 42.4 (s, C-10), 42.5 (br s, C-9), 120.0 (qdd, $^1J_{CF}$ 271, $^2J_{CF}$ 35, $^3J_{CF}$ 9.6, CF_3), 135.8 (dqd, $^1J_{CF}$ 250, $^2J_{CF}$ 40, $^2J_{CF}$ 24, *C*FCF$_3$), 154.9 (ddq, $^1J_{CF}$ 266, $^2J_{CF}$ 9.4, $^3J_{CF}$ 3.4, CH*C*F); *m*/*z* (EI$^+$) 268 (M^+, 17%), 95 (51), 81 (100), 67 (92), 41 (47).

x-(1,1,2,3,3,3-Hexafluoropropyl)-*cis*-decahydronaphthalene (x = 1, 2, 9). x-(1,1,2,3,3,3-Hexafluoropropyl)-*cis*-decahydronaphthalene (x = 1, 2, 9) **25** (5.8 g, 20 mmol) was added to sodium *tert*-butoxide (4.5 g, 40 mmol) in dry diethyl ether (40 ml), cooled to −10 °C, and stirred for 30 minutes. Fractional distillation gave an isomeric mixture of 2-[(1*Z*)-pentafluoroprop-1-enyl]-*cis*-decahydronaphthalene (x = 1, 2, 9) **43** (4.6 g,

85%), bp^{20} 138–140 °C (Found: C, 58.1; H, 6.3. $C_{13}H_{17}F_5$ requires C, 58.2; H, 6.3%); 2-[(1*Z*)-pentafluoroprop-2-enyl]-*cis*-decahydronaphthalene **43b** δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.29 to 1.84 (16 H, overlapping m, CH + CH_2), 2.65 (1 H, dm, $^3J_{HF}$ 36, CHCF); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −66.2 (3 F, br s, CF_3), −131.3 (1 F, d, $^3J_{HF}$ 36, CHCF), −161.3 (1 F, br s, $CFCF_3$); δ_C (100 MHz; $CDCl_3$; Me_4Si) 20.8 (s, C-6), 25.6 (s, C-7), 28.1 (d, $^5J_{CF}$ 2.7, C-3), 28.9 (s, C-5), 31.3 (dm, $^2J_{CF}$ 21, C-2), 32.2 (s, C-4), 34.9 (d, $^5J_{CF}$ 2.3, C-1), 35.2 (s, C-10), 35.3 (s, C-9), 120.4 (qdd, $^1J_{CF}$ 270, $^2J_{CF}$ 35, $^3J_{CF}$ 9.6, CF_3), 134.9 (dqd, $^1J_{CF}$ 248, $^2J_{CF}$ 40, $^2J_{CF}$ 24, *C*FCF$_3$), 156.7 (ddq, $^1J_{CF}$ 266, $^2J_{CF}$ 9.6, $^3J_{CF}$ 3.4, CH*C*F); *m*/*z* (EI$^+$) 268 (M$^+$, 12%), 135 (67), 95 (98), 41 (100), 39 (77); 1-[(1*Z*)-pentafluoroprop-1-enyl]-*cis*-decalin **43a** δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.29 to 1.84 (16 H, overlapping m, CH + CH_2), 2.58 (1 H, dm, $^3J_{HF}$ 32, CHCF); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −66.2 (3 F, br s, CF_3), −132.2 (1 F, d, $^3J_{HF}$ 32, CHCF), −161.5 (1 F, br s, $CFCF_3$); δ_C (100 MHz; $CDCl_3$; Me_4Si) 20.9 (s, C-6), 23.1 (d, $^5J_{CF}$ 2.6, C-2), 24.9 (s, C-7), 26.1 (s, C-3), 27.0 (s, C-5), 32.1 (s, C-4), 35.7 (s, C-10), 35.9 (s, C-9), 37.3 (dm, $^2J_{CF}$ 21, C-1), 120.4 (qdd, $^1J_{CF}$ 270, $^2J_{CF}$ 35, $^3J_{CF}$ 9.6, CF_3), 134.8 (dqd, $^1J_{CF}$ 248, $^2J_{CF}$ 40, $^2J_{CF}$ 24, *C*FCF$_3$), 156.5 (ddq, $^1J_{CF}$ 265, $^2J_{CF}$ 9.6, $^3J_{CF}$ 3.4, CH*C*F); *m*/*z* (EI$^+$) 268 (M$^+$, 14%), 95 (42), 81 (100), 67 (49), 41 (52); 9-[(1*Z*)-pentafluoroprop-1-enyl]decalin **43c** δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.29 to 1.84 (17 H, overlapping m, CH + CH_2); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −65.7 (3 F, m, CF_3), −134.2 (1 F, d, *J* 30, CHCF), −160.1 (1 F, s, $CFCF_3$); δ_C (100 MHz; $CDCl_3$; Me_4Si) 20.6 (s, C-3/6), 26.7 (s, C-2/7), 29.0 (s, C-4/5), 32.5 (br s, C-1/8), 34.0 (dm, $^2J_{CF}$ 21, C-9), 36.1 (s, C-10), 120.4 (m, CF_3), 136.0 (m, *C*FCF$_3$), 155.9 (m, C*C*F); *m*/*z* (EI$^+$) 268 (M$^+$, 13%), 95 (50), 81 (87), 67 (100), 41 (88).

***exo*-2-(1,1,2,3,3,3-Hexafluoropropyl)bicyclo[2.2.1]heptane.** *exo*-2-(1,1,2,3,3,3-Hexafluoropropyl)bicyclo[2.2.1]heptane **28** (7.5 g, 30 mmol) was added to sodium *tert*-butoxide (6.8 g, 60 mmol) in dry diisopropyl ether (20 ml) cooled to −10 °C, and stirred for 1 hour. Fractional distillation gave *exo*-2-[(1*Z*)-pentafluoroprop-1-enyl]bicyclo[2.2.1]heptane **44** (6.2 g, 90%) bp^{20} 65–67 °C (Found: C, 53.1; H, 4.9. $C_{10}H_{11}F_5$ requires C, 53.1; H, 4.9%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.25 (3 H, m, CH_2), 1.57 (4 H, m, CH_2), 1.71 (1 H, m, CH_2), 2.35 (2 H, s, CH), 2.54 (1 H, dm, $^3J_{HF}$ 36, CHCF); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −67.1 (3 F, br s, CF_3), −130.7 (1 F, d, $^3J_{HF}$ 36, CHCF), −162.2 (1 F, br s, $CFCF_3$); δ_C 27.9 (s, C-6), 30.3 (s, C-5), 34.7 (s, C-3), 36.1 (s, C-4), 37.4 (s, C-7), 38.8 (dm, $^2J_{CF}$ 21, C-2), 42.0 (d, $^5J_{CF}$ 3.2, C-1), 120.2 (qdd, $^1J_{CF}$ 270, $^2J_{CF}$ 35, $^3J_{CF}$ 9.6, CF_3), 134.5 (dqd, $^1J_{CF}$ 250, $^2J_{CF}$ 40, $^2J_{CF}$ 25, *C*FCF$_3$), 156.5 (ddq, $^1J_{CF}$ 265, $^2J_{CF}$ 9.6, $^3J_{CF}$ 3.4, CH*C*F); *m*/*z* (EI$^+$) 226 (M$^+$, 4%), 139 (10), 68 (100), 67 (35).

***exo*-2,x-Bis(1,1,2,3,3,3-hexafluoropropyl)bicyclo[2.2.1]-heptane (x = 5, 6).** *exo*-2,x-Bis(1,1,2,3,3,3-hexafluoropropyl)-bicyclo[2.2.1]heptane (x = 5, 6) **29** (4.6 g, 12 mmol) was added to sodium *tert*-butoxide (4.5 g, 40 mmol) in dry diisopropyl ether (15 ml), cooled to −10 °C, and stirred for 30 minutes. Fractional distillation gave an isomeric mixture of *exo*-2,x-bis[(1*Z*)-pentafluoroprop-1-enyl]bicyclo[2.2.1]heptane (x = 5, 6) **45** (3.8 g, 93%) bp^{20} 101–103 °C (Found: C, 43.6; H, 2.8. $C_{13}H_{10}F_{10}$ requires C, 43.8; H, 2.8%); *exo*-2,5-bis[(1*Z*)-pentafluoroprop-1-enyl]bicyclo[2.2.1]heptane **45a** δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.65 (2 H, m, CH_2), 1.83 (2 H, m, CH_2), 2.50 (2 H, m, CH), 2.61 (2 H, m, CHCF); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −66.0 (3 F, m, CF_3), −130.5 (1 F, d, $^3J_{HF}$ 32, CHCF), −159.3 (1F, br s, C*F*CF$_3$); δ_C (100 MHz; $CDCl_3$; Me_4Si) 35.2 (s, C-3/6), 37.0 (s, C-7), 38.0 (dd, $^2J_{CF}$ 21, $^3J_{CF}$ 2.6, C-2/5), 41.9 (d, $^3J_{CF}$ 2.6, C-1/4), 120.5 (qdd, $^1J_{CF}$ 270, $^2J_{CF}$ 35, $^3J_{CF}$ 9.6, CF_3), 135.3 (dqd, $^1J_{CF}$ 251, $^2J_{CF}$ 40, $^2J_{CF}$ 25, *C*FCF$_3$), 155.2 (ddq, $^1J_{CF}$ 266, $^2J_{CF}$ 11, $^3J_{CF}$ 3.4, CH*C*F); *m*/*z* (EI$^+$) 356 (M$^+$, 3%), 198 (85), 139 (47), 129 (100); *exo*-2,6-bis[(1*Z*)-pentafluoroprop-1-enyl]bicyclo[2.2.1]-heptane **45b** δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.65 (4 H, m, CH_2), 1.86 (2 H, m, CH_2), 2.46 (1 H, m, CH_2), 2.53 (1 H, m, CH), 2.63 (2 H, dm, $^3J_{HF}$ 36, CHCF); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −66.0 (3 F, br s, CF_3), −128.7 (1 F, d, $^3J_{HF}$ 36, CHCF), 158.6 (1 F, br s, C*F*712;CF_3); δ_C (100 MHz; $CDCl_3$; Me_4Si) 33.1 (s, C-3/5), 36.2 (s, C-4), 36.5 (s, C-7), 41.9 (dm, $^2J_{CF}$ 20, C-2/6), 48.2 (s, C-1), 120.4 (qdd, $^1J_{CF}$ 269, $^2J_{CF}$ 35, $^3J_{CF}$ 9.4, CF_3), 135.7 (dqd, $^1J_{CF}$ 252, $^2J_{CF}$ 40, $^2J_{CF}$ 25, *C*FCF$_3$), 154.8 (ddq, $^1J_{CF}$ 267, $^2J_{CF}$ 11, $^3J_{CF}$ 3.4, CH*C*F); *m*/*z* (EI$^+$) 356 (M$^+$, 3%), 198 (80), 139 (49), 129 (100).

1-(1,1,2,3,3,3-Hexafluoropropyl)adamantane. 1-(1,1,2,3,3,3-Hexafluoropropyl)adamantane **31** (11.4 g, 40 mmol) was added to sodium *tert*-butoxide (7.9 g, 70 mmol) in dry diisopropyl ether (50 ml) at room temperature, and stirred for 30 minutes. Fractional distillation gave 1-[(1*E*)-pentafluoroprop-1-enyl]adamantane **46b** (9.6 g, 90%) bp 219–221 °C (Found: C, 58.6; H, 5.9. $C_{13}H_{15}F_5$ requires C, 58.6; H, 5.6%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.77 (6 H, br s, CH_2), 1.97 (6 H, br s, CH_2), 2.06 (3 H, br s, CH); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −67.6 (3 F, d, $^4J_{F\text{-}F}$ 22, CF_3), −149.3 (1 F, dq, $^3J_{FF}$ 131, $^4J_{FF}$ 22, CCF), −175.6 (1 F, d, $^3J_{FF}$ 131, $CFCF_3$); δ_C (100 MHz; $CDCl_3$; Me_4Si) 27.8 (s, CH_2), 36.3 (s, CH), 37.8 (m, CH_2), 119.5 (qdd, $^1J_{CF}$ 273, $^2J_{CF}$ 36, $^3J_{CF}$ 3.5, CF_3), 138.2 (dqd, $^1J_{CF}$ 242, $^2J_{CF}$ 54, $^2J_{CF}$ 39, *C*FCF$_3$), 160.2 (ddq, $^1J_{CF}$ 260, $^2J_{CF}$ 36, $^3J_{CF}$ 2.3, C*C*F); *m*/*z* (EI$^+$) 266 (M$^+$, 80%), 94 (98), 93 (100), 79 (89), 41 (95).

1-(1,1,2,3,3,3-Hexafluoropropyl)adamantane. 1-(1,1,2,3,3,3-Hexafluoropropyl)adamantane **31** (3.8 g, 13 mmol) was added to sodium *tert*-butoxide (3.2 g, 28 mmol) in dry diisopropyl ether (50 ml) at −10 °C, and stirred for 30 minutes. Fractional distillation gave 1-[(1*Z*)-pentafluoroprop-1-enyl]adamantane **46a** (3.0 g, 85%) bp 219–221 °C (Found: C, 58.7; H, 5.4. $C_{13}H_{15}F_5$ requires C, 58.6; H, 5.6%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 1.77 (6 H, br s, CH_2), 1.94 (6 H, br s, CH_2), 2.07 (3 H, br s, CH); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −59.9 (3 F, br s, CF_3), −125.2 (1 F, br s, CCF), −154.7 (1 F, br s, C*F*CF$_3$); δ_C (100 MHz; $CDCl_3$; Me_4Si) 27.9 (s, CH_2), 36.2 (s, CH), 37.1 (dm, $^2J_{CF}$ 21, *C*CF), 38.0 (q, $^3J_{CF}$ 2.3, CH_2), 120.1 (qdd, $^1J_{CF}$ 270, $^2J_{CF}$ 36, $^3J_{CF}$ 8.4, CF_3), 137.8 (dqd, $^1J_{CF}$ 249, $^2J_{CF}$ 43, $^2J_{CF}$ 30, *C*FCF$_3$), 160.7 (dd, $^1J_{CF}$ 260, $^2J_{CF}$ 13, CH*C*F); *m*/*z* (EI$^+$) 266 (M$^+$, 18%), 94 (100), 93 (97), 79 (65), 41 (57).

1,3,5,7-Tetrakis(1,1,2,3,3,3-hexafluoropropyl)adamantane. 1,3,5,7-Tetrakis(1,1,2,3,3,3-hexafluoropropyl)adamantane **34** (3.7 g, 5 mmol) in dry diethyl ether (20 ml) was added to sodium *tert*-butoxide (4.5 g, 40 mmol) in dry diethyl ether (30 ml) and stirred at room temperature. Kugelrohr distillation gave an isomeric mixture of 1,3,5,7-tetrakis(pentafluoroprop-1-enyl)-adamantane **47**, **48** (2.6 g, 78%) bp^1 175 °C (Found: C, 40.2; H, 1.8. $C_{22}H_{12}F_{20}$ requires C, 40.3; H, 1.8%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 2.18 (6 H, br s, CH_2), 2.19 (6 H, br s, CH_2); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −60.4 (3 F, br s, CF_3), −68.5 (9 F, br s, CF_3), −126.7 (1 F, br s, CCF), −148.6 (1 F, br s, C*F*CF$_3$), −150.6 (3 F, m, CCF), −171.6 (3 F, d, $^3J_{FF}$ 135, $CFCF_3$); *m*/*z* (EI$^+$) 656 (M$^+$, 10%), 145 (100), 95 (66), 69 (51); from which 1,3,5,7-tetrakis[(1*E*)-pentafluoroprop-1-enyl]-adamantane **47** δ_H (250 MHz; $CDCl_3$; Me_4Si) 2.21 (12 H, br s, CH_2); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −67.6 (12 F, d, $^4J_{FF}$ 23, CF_3), −149.7 (3 F, dq, $^3J_{FF}$ 134, $^4J_{FF}$ 23, CCF), −170.3 (3 F, dq, $^3J_{FF}$ 134, $^3J_{FF}$ 9.4, $CFCF_3$); δ_C (100 MHz; $CDCl_3$; Me_4Si) 36.4 (s, CH_2), 118.8 (qdd, $^1J_{CF}$ 273, $^2J_{CF}$ 36, $^3J_{CF}$ 3.4, CF_3), 139.7 (dqd, $^1J_{CF}$ 248, $^2J_{CF}$ 52, $^2J_{CF}$ 40, *C*FCF$_3$), 156.1 (dd, $^1J_{CF}$ 261, $^2J_{CF}$ 39, C*C*F); *m*/*z* (EI$^+$) 656 (M$^+$, 5%), 145 (100), 95 (73), 69 (56) crystallised out when the mixture was dissolved in chloroform and cooled in an acetone–carbon dioxide bath (−78 °C).

Conversion of 1-[(1*Z*)-pentafluoroprop-1-enyl]adamantane. A Carius tube was charged with caesium fluoride (7.6 g, 50 mmol), dry tetraglyme (10 ml) and 1-[(1*Z*)-pentafluoroprop-2-

Table 8 Crystal data

Compound	**20a**	**34**	**41a**	**47**
Formula	$C_{12}H_{12}F_{12}$	$C_{22}H_{16}F_{24}$	$C_{12}H_{10}F_{10}$	$C_{22}H_{12}F_{20}$
Formula weight	384.2	736.4	344.2	656.3
T/K	293	150	150	293
Crystal system	triclinic	orthorhombic	monoclinic	monoclinic
a/Å	6.365(4)	11.442(8)	15.006(13)	15.758(3)
b/Å	6.829(3)	14.992(14)	7.217(4)	15.951(3)
c/Å	8.949(5)	15.011(10)	6.223(5)	19.896(4)
α/°	71.54(4)	90	90	90
β/°	82.58(6)	90	102.74(7)	93.21(1)
γ/°	89.22(5)	90	90	90
V/Å^3	365.7(3)	2575(3)	657.4(9)	4993(2)
Space group	$P\bar{1}$ (#2)	$Pnma_1$ (#62)	$C2/m$ (#12)	$I2/a$ (#15)
Z	1	4	2	8
λ/Å	0.71073	0.71073	0.71073	1.54184
μ/mm^{-1}	0.21	0.23	0.20	
D_{calc}/g cm^{-3}	1.745	1.90	1.74	
Reflections total	655	10933	1042	
Max. 2θ/°	40	51	55	
Unique refls.	578	2348	816	
Refls. with $I > 2\sigma(I)$	335	1558	672	
R_{int}	0.026	0.040	0.014	
No. of variables	79	250	88	
w$R(F^2)$, all data	0.118	0.357	0.114	
$R[I > 2\sigma(I)]$	0.037	0.119	0.044	
$\Delta\rho_{max,min}$/e Å^{-3}	0.15, −0.21	0.62, −0.63	0.26, −0.23	

enyl]adamantane **46a** (2.7 g, 10 mmol). The tube was cooled (liquid air) and sealed under vacuum. It was allowed to warm to room temperature and then it was heated in a rotating oil bath at 200 °C for 50 h. On completion the tube was opened and a sample of the product mixture was transferred into an NMR tube and a ^{19}F NMR spectrum was recorded, which showed almost complete conversion to 1-[(1*E*)-pentafluoroprop-1-enyl]adamantane **46b** (*ca.* 97% by ^{19}F NMR).

1-(1,1,2,3,3,3-Hexafluoropropyl)adamantane. A sealable NMR tube, cooled in liquid air, was charged with sodium *tert*-butoxide (0.1 g, 0.6 mmol), *tert*-butanol (D) (2-methylpropan-2-ol, *ca.* 1 ml) and 1-(1,1,2,3,3,3-hexafluoropropyl)adamantane **31** (0.3 g, 1 mmol). The tube was allowed to warm to room temperature and then left for a further 15 minutes at 25 °C. A ^{19}F NMR spectrum was then recorded on the contents, which indicated 2D-hexafluoropropyladamantane **31a** (9% by ^{19}F NMR spectroscopy); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −207.5 (br s, CFD).

General procedure for fluorinations with cobalt trifluoride

The apparatus for fluorination with cobalt trifluoride consisted of a nickel tube with inlet and outlet pipes and nickel paddles attached to a rod situated along the axis of the tube and rotated by an electric motor. Cobalt trifluoride (440 g) was contained in the tube and heated to the required temperature, using an electric heating tape wrapped around the tube, with continuous stirring. Dry nitrogen (30 ml min^{-1}) was passed through the reactor for 10 min, prior to use. Starting materials were fed into the reactor at a rate of 0.1 ml min^{-1} in a nitrogen flow (30 ml min^{-1}). After all the compound for fluorination was added, the reactor was flushed with nitrogen for 30 min. Products were collected in a trap cooled with liquid air, which was then detached from the reactor and left to warm up in a fume cupboard. A condenser containing anhydrous soda-lime was attached to the trap, so as to remove any hydrogen fluoride evolved and the product was pipetted out. Any hydrogen-containing products were removed by continuous extraction with acetone and pure samples of the perfluorinated product were isolated by preparative GC. After use, the cobalt fluoride system was regenerated by passing 50% fluorine gas (95 ml min^{-1}), from a cylinder, *via* FEP tubing through the heated reactor (280 °C) until the soda-lime trap, attached to the exit, became detectably warm.

(1,1,2,3,3,3-Hexafluoropropyl)cyclopentane. (1,1,2,3,3,3-Hexafluoropropyl)cyclopentane **16** (3.9 g, 18 mmol), was passed through the cobalt trifluoride reactor, at 375 °C, to give a colourless liquid (6.1 g). Continuous extraction followed by preparative GC gave perfluoropropylcyclopentane **49** (3.7 g, 60%) bp 103–105 °C; δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −81.2 (3 F, s, CF_3), −116.1 (2 F, s, CF_2), −123.0 and −128.3 (4 F, AB, J_{AB} 268, CF_2), −125.1 (2 F, s, CF_2), −129.0 and −132.5 (4 F, AB, J_{AB} 259, CF_2), −185.2 (1 F, s, CF); *m*/*z* (EI$^+$) 381 (1%), 281 (32), 181 (33), 131 (70), 69 (100).

1,x-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclopentane, (x = 2, 3). 1,x-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclopentane (x = 2, 3) **17** (5.0 g, 14 mmol), was passed through the cobalt trifluoride reactor, at 375 °C, to give a colourless liquid (5.7 g). Continuous extraction followed by preparative GC gave an isomeric mixture of perfluoro-1,x-di-*n*-propylcyclopentane (x = 2,3) **50** (4.0 g, 71%) bp 159–161 °C; δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −83.31 (12 F, m, $4CF_3$), −114.2 to −134.4 (28 F, overlapping m, $14CF_2$), −183.9 (2 F, s, 2CF), −185.9 (2 F, s, 2CF); *m*/*z* (EI$^+$) 531 (5%), 431 (13), 281 (70), 181 (68), 169 (67), 131 (87), 69 (100).

(1,1,2,3,3,3-Hexafluoropropyl)cyclohexane. (1,1,2,3,3,3-Hexafluoropropyl)cyclohexane **19** (3.5 g, 15 mmol) was passed through the cobalt trifluoride reactor, at 375 °C, to give a colourless liquid (6.0 g). Continuous extraction followed by preparative GC gave perfluoropropylcyclohexane **51** (3.8 g, 63%) bp 132–134 °C; δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −80.6 (3 F, s, CF_3), −112.3 (2 F, s, CF_2), −118.2 and −128.9 (4 F, AB, J_{AB} 302, CF_2), −121.9 and −139.9 (4 F, AB, J_{AB} 287, CF_2), −123.9 and −142.2 (4 F, AB, J_{AB} 289, CF_2), −128.4 (2 F, s, CF_2), −185.6 (1 F, s, CF); *m*/*z* (EI$^+$) 431 (3%), 181 (15), 169 (14), 131 (49), 69 (100) in agreement with the literature.[22]

[(1*Z*)-Pentafluoro-1-propenyl]cyclohexane. [(1*Z*)-Pentafluoro-1-propenyl)cyclohexane **40** (4.0 g, 19 mmol) was passed through the cobalt trifluoride reactor, at 375 °C, to give a

colourless liquid (7.1 g). Preparative GC gave perfluoropropylcyclohexane **51** (6.4 g, 90%).

***trans*-1,4-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane.** *trans*-1,4-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane **20a** (2.4 g, 6 mmol) was passed through the cobalt trifluoride reactor, at 400 °C, to give a colourless liquid (2.9 g). Preparative scale GC gave a mixture of *cis*- and *trans*-isomers of perfluoro-1,4-dipropylcyclohexane **52** (1.9 g, 65%); *cis*-perfluoro-1,4-dipropylcyclohexane δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −81.0 (6 F, s, CF_3), −113.4 (4 F, s, CF_2), −119.4 (4 F, s, CF_2), −124.8 (8 F, br s, CF_2), −183.0 (2 F, br s, CF); *m*/*z* (EI^+) 481 (4%), 331 (20), 181 (21), 169 (100), 131 (27), 119 (37), 69 (46); *trans*-perfluoro-1,4-dipropylcyclohexane mp 80–81 °C (from $CFCl_3$); δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −81.2 (6 F, br s, CF_3), −117.7 and −126.7 (8 F, AB, J_{AB} 297, CF_2), −119.4 (4 F, s, CF_2), −126.7 (4 F, s, CF_2), −186.7 (2 F, s, CF); *m*/*z* (EI^+) 481 (4%), 331 (16), 181 (21), 169 (100), 131 (21), 119 (26), 69 (69).

1,x-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (x = 3, 4). 1,x-Bis(1,1,2,3,3,3-hexafluoropropyl)cyclohexane (x = 3, 4) **20** (5.0 g, 13 mmol), was passed through the cobalt trifluoride reactor, at 375 °C, to give a colourless liquid (6.5 g). Continuous extraction followed by preparative scale GC gave an isomeric mixture of perfluoro-1,x-dipropylcyclohexane **53** (x = 3, 4) (3.8 g, 58%) bp 167–169 °C; δ_F (235 MHz; $CDCl_3$; $CFCl_3$) −80.9 (24 F, m, CF_3), −109.7 to −139.4 (64 F, overlapping m, CF_2), −182.52 (2F, s, 2CF), −182.81 (2F, s, 2CF), −184.35 (2 F, s, 2CF), −184.25 (2 F, s, 2CF); *m*/*z* 481 (5%), 331 (17), 181 (30), 169 (100), 131 (42), 119 (44), 69 (87).

Crystallographic studies

Single-crystal X-ray diffraction experiments for **20a**, **41a** and **47** were carried out on a Rigaku AFC6S 4-circle diffractometer, using graphite-monochromated Mo-Kα radiation or (for **47**) Cu-Kα radiation. Data were collected in a $2\theta/\omega$ scan mode (**17a**), ω scans with Lehmann–Larsen profile analysis (**41a**) or ω scan mode (**47**). **20a** and **47** showed a significant decay of intensities during data collection, by 16% and 9% respectively. For **34**, the experiment was performed with a SMART 1K CCD area detector mounted on a 3-circle diffractometer (Mo-Kα radiation). Four sets of ω scans, each at different φ and/or 2θ angles, nominally covered over a hemisphere of reciprocal space. A Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat was used for low temperature experiments (**34**, **41a**). The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software.[23] All crystals gave exceedingly weak high-angle reflections and were prone to cracking on cooling, hence rather low resolution. Compound **47** did not give satisfactory data for atomic resolution, although the electron density map is in agreement with the expected molecular structure. Crystal data and experimental parameters are listed in Table 8. CCDC reference number 207/408. See http://www.rsc.org/suppdata/p1/a9/a909777e for crystallographic files in .cif format.

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