Free Radical Chemistry. Part 3.[1] Substituent Effects in Additions of Ethers to Fluorinated Alkenes

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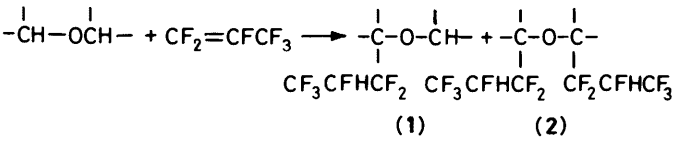
Systematic studies on free-radical additions of acyclic ethers to hexafluoropropene reveal the influence of steric effects on the competitive formation of mono-, di-, and tri-adducts. It is concluded that 'capto-dative' effects are not dominant in systems containing polyfluoroalkyl groups. Remarkably efficient free-radical additions of trialkyl borates, to fluorinated alkenes occur, but in a series X-OMe (X = MeCO, HCO, MeOCO *etc.*) reactivity is reduced by electron withdrawal.

It is well known[2–4] that fluorinated alkenes participate in a range of free-radical addition reactions with ethers, alcohols, aldehydes *etc.* Development of the use of the carbon–hydrogen bond as a functional group is, of course, very important, and we have a particular interest in this process for the synthesis of a variety of derivatives containing fluorocarbon groups. Moreover, it will become clear that these systems provide a useful probe for pursuing the effects of substituents in free radical processes. In our view, the ability to predict the effect on reactivity of relatively simple changes in structure, is often strangely lacking for many simple radical reactions, in comparison with the now highly confident approach of the synthetic chemist to ionic processes (*e.g.* see major text-books in organic chemistry). This highlights the relative dearth of systematic studies of structure and reactivity in radical reactions from the point of view of the synthetic rather than the physical chemist. This paper, is concerned with additions of acyclic ethers and related derivatives to highly fluorinated alkenes, principally hexafluoropropene. A number of investigations are reported in the literature,[5–7] involving free-radical additions of a limited number of ethers to hexafluoropropene, and mono- (**1**) and di- (**2**) addition products have been described, depending on the system used.



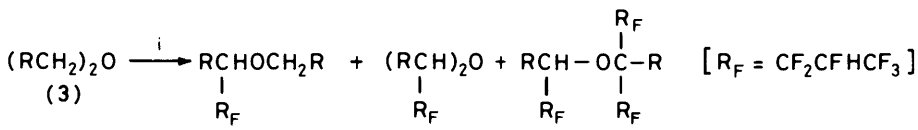
Scheme 1.

Both types of product (**1**) and (**2**) were obtained from diethyl ether[5] and partly fluorinated derivatives of diethyl ether,[6] while mono-addition products (**1**) were obtained from dimethyl ether under photochemical and thermal conditions.[7]

We have systematically studied γ-ray initiated additions of a series of acyclic ethers and related compounds to hexafluoropropene, under a standard set of conditions (see Experimental section), and this enables us to compare substituent effects on the reactivity of the ether. These comparisons are based on percentage conversions that are presented in Table 1, and from this it can be seen that di-isopropyl ether undergoes a surprisingly low conversion to addition products. Also mixtures of mono- (**4b**), (**4c**) and bis- (**5b**), (**5c**) adducts were obtained from diethyl and dipropyl ether respectively, in contrast with dimethyl ether, which gave only mono-adduct (**4a**), and dibutyl ether, which gave a large proportion of the tri-adduct (**6d**).

The influence of the oxygen atom on formation of radicals from ethers has been discussed by other workers[8] and, in simple terms, we may represent the stabilising effect of oxygen as in (**7**). Katritzky and co-workers[9] have emphasised the stabilising effect of a combination of donor and acceptor groups being attached to a radical centre ('merostabilisation') and Viehe and co-workers[10] have taken this concept further ('capto-dative stabilisation') and impressively illustrated the wide-ranging influence of the phenomenon. Most of these examples, however, incorporate a *conjugatively* electron-withdrawing group and it remains to be demonstrated that an *inductively* electron-

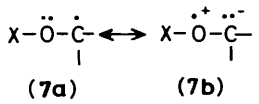
Table 1.



	Products (% Composition)			% Conversion[a,b]
(3a) R = H	(4a) (100)	–	–	70
(3b) R = Me	(4b) (47)	(5b) (53)	–	100
(3c) R = Et	(4c) (30)	(5c) (70)	–	80
(3d) R = Pr^n	(4d) (23)	(5d) (40)	(6d) (37)	70

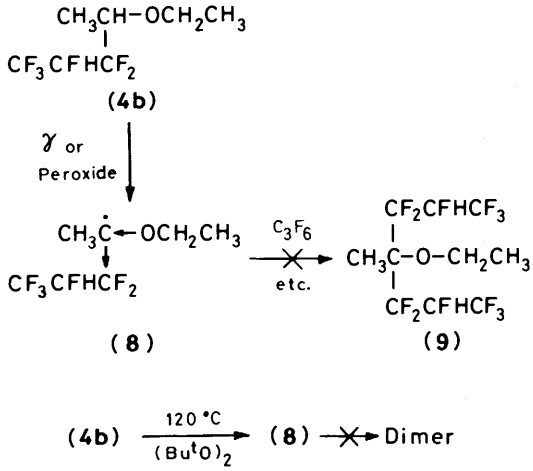
Reagents: i, CF_2=$CFCF_3$, γ-rays, sealed evacuated tube, 18 °C, excess of ether. [a] Based on hexafluoropropene consumed. [b] $(Pr^i)_2O$ —i→ very low conversion to unidentified products

withdrawing group can participate effectively in a 'capto-dative' system. In principle, adducts of type (**1**) provide an effective test for such substituents *e.g.* adduct (**4b**) could give a radical (**8**), which has the opportunity of capto-dative stabilisation, which would then lead to bis-adduct (**9**). However, the di-adduct actually formed from (**5**) has the structure (**5b**) (see Scheme 1) and in addition, it was very difficult to produce the di-adduct

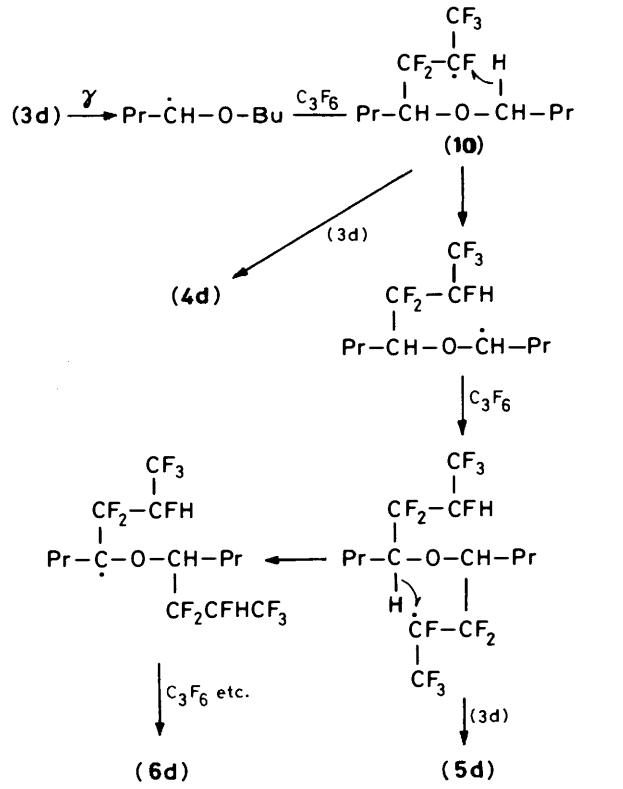


(**7a**) (**7b**)

(**5b**) from (**4b**) directly. Furthermore Viehe and co-workers[10,11] have produced a number of coupling reactions of capto-dative systems, using peroxides but, in contrast, we have been unable to couple compounds such as (**4b**),—*via* radical (**8**)—by heating

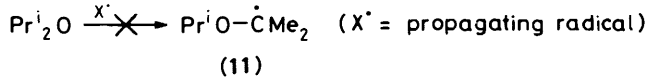


with t-butyl peroxide. Therefore, these results point against the capto-dative effect being important for systems involving these *inductively* electron-withdrawing groups. Indeed, rather than activating the system towards further reaction, introduction of a perfluoroalkyl group clearly *deactivates* sites adjacent to oxygen, towards further free-radical attack, a conclusion reached earlier by Muramatsu and co-workers.[6] This may now be accounted for by considering (**7**) since, when X is electron-withdrawing, then the ability to donate, as represented by (**7b**), is clearly diminished. The low reactivity of mono-adducts (**1**) towards fluorinated alkenes has been reasonably taken[6] as strong evidence that the formation of di-adducts (**2**) occurs *via* an intramolecular hydrogen transfer process. Consequently, the formation of the tri-adduct (**6d**) as a major product even in the presence of remaining dibutyl ether, is a spectacular illustration of this process (see Scheme 2). Competition of the intermolecular formation of the mono-adduct (**4d**) with the intramolecular step which leads to the di-adduct (**5d**), shown in Scheme 2, is clearly affected by the chain length of the ether, but the reason for this is not immediately obvious. The most reasonable explanation seems to be that of a simple steric effect, *i.e.* that in the intermediate radical (**10**), the sterically demanding alkyl chains inhibit the intermolecular reaction with ether, to give the mono-adduct (**4d**) and consequently allows the intramolecular process to compete more effectively. It is also probable that increased chain lengths favours conformations for (**10**) which assist the [1,5]-H transfer steps, which eventually



Scheme 2.

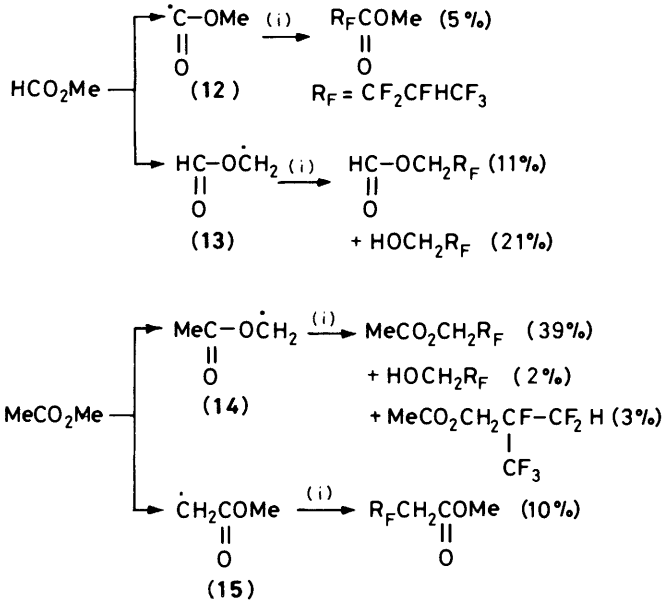
lead to the tri-adduct (**6d**). A steric argument may also be applied to account for the surprising lack of reactivity of di-isopropyl ether which, in principle, should give the more stable radical (**11**). However, the propagating radicals (X·) are



(**11**)

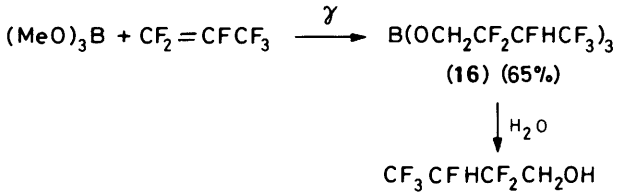
relatively bulky and it seems likely that attack on di-isopropyl ether is inhibited for simple steric reasons.

We have subsequently examined a series of systems that correspond to the general structure X-O-Me, in order to compare the effect of the nature of X on production of radicals (**7**) and their subsequent reactivity towards fluoroalkenes. Using γ-rays at room temperature, negligible conversion was observed for the systems where X = MeCO, HCO, MeOCO, $MeOCOCH_2CO$, Ph, and ClCO, implying that all electron-withdrawing groups deactivate for reasons that have been outlined above in relation to (**7**). At higher temperatures (using di-t-butyl peroxide as the initiator) products were obtained from the systems where X = HCO (total yield 37%), MeCO (54%), and MeOCO (55%). In the case of methyl formate we have in competition the formation of radicals (**12**) and (**13**) but, clearly, the route *via* (**13**) is preferred. Similarly, methyl acetate could lead to radicals (**14**) or (**15**) but (**14**) is preferred. In the latter case a small amount of reverse addition to hexafluoropropene was observed and this behaviour has been noted previously for other radicals with electron-withdrawing substituents.[12] In both reactions, some alcohol was observed and this seems to arise from peroxide-initiated decarbonylation of the partly fluorinated esters.

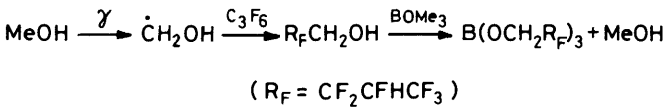


Scheme 3. *Reagents*; i, D.T.B.P, 120 °C.

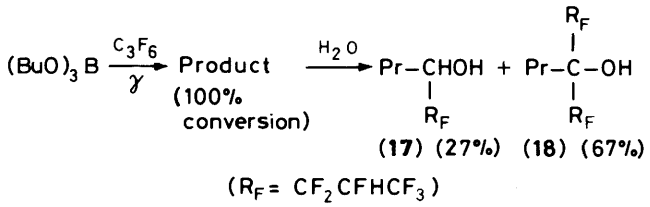
For comparison, we have also studied free-radical reactions of trimethyl borate with hexafluoropropene, *i.e.* a system X-OMe where X = $(MeO)_2B$ and, therefore, a very powerful conjugatively electron-withdrawing group. It was surprising, therefore, to find that hexafluoropropene reacted extremely efficiently at room temperature. We have also found that perfluorocyclo-butene, -pentene, and-hexene reacted readily to



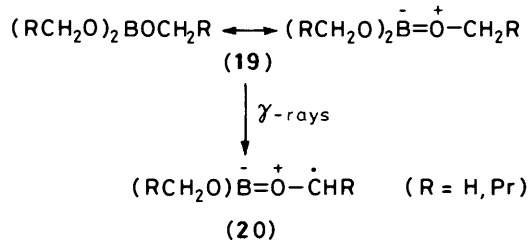
give analogous products and these products were additionally characterised by hydrolysis to the corresponding alcohols. There exists, however, a potential ambiguity in the mechanism of these reactions because a possible process involves free-radical addition of the methanol impurity in the ester, followed by exchange to give the fluorinated borate esters. Consequently, we have taken extreme precautions to remove methanol and moisture from our systems and found that the conversion to the product was not dependent on the presence of methanol. More



importantly, however, we were also able to carry out efficient additions to hexafluoropropene using tributyl borate; the significance of this is that the latter ester is readily distilled apart from the alcoholic impurity. The products in this case were more complicated and were identified by conversion into the alcohols (**17**) and (**18**). It seems inconceivable that such highly

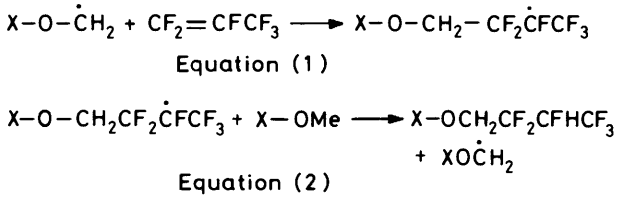


efficient processes should proceed *via* minute traces of the alcohol and we are left with the conclusion that boron *promotes*, rather than inhibits, the production of a radical at the attached alkoxy site. A simple way of describing the effect of boron would be that it participates in a pseudo-allylic system (**19**) leading to the radical (**20**) in which the unpaired electron is in an orbital



extending to include B–O–C. Simply viewed as another electron-withdrawing substituent in the X-O-CH_2R system, boron would be massively inhibiting to these additions to fluorinated alkenes.

So far, we have assumed that the effect of substituents in the ethers has been principally on the propagation step [equation (2)] rather than the addition step [equation (1)]. Evidence that

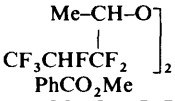


this is valid has been sought from reactions of other radicals with the series X-OMe. In particular, other workers[13–15] have measured the acetone–t-butyl alcohol ratios for the decomposition of $(Bu^tO)_2$ in various systems and related these ratios to the ease of hydrogen abstraction. Acetone–t-butyl alcohol ratios have been determined for the series of derivatives X-OMe contained in Table 2 and there is a quite clear relationship between these ratios and reactivity towards hexafluoropropene. We may conclude, therefore, that the substituent effects that have been described above, for reactions with hexafluoropropene, relate to the ease of hydrogen abstraction as outlined in Equation (2).

Experimental

Distillations were carried out using a Fischer-Spaltrohr MS200 apparatus. Boiling points were recorded by the Siwoloboff method or during distillation and are uncorrected. Quantitative g.l.c. analyses were carried out using a Varian Aerograph Model 920 equipped with a gas density balance detector and columns packed with di-isodecyl phthalate (20%) on Chromosorb P or

Table 2. Acetone–t-butyl alcohol ratios for the decomposition of $(Bu^tO)_2$ in various solvents

Solvent	[Acetone]–[Bu^{t}OH]
	>100
$PhCO_2Me$	2.9
Me–CH(O–Et)–CF_3CHFCF_2	2.4
Pr^i_2O	2.2
$MeCO_2Me$	1.9
$(ClCH_2CH_2)_2O$	1.6
PhOMe	0.4↑A*
Bu_2O	0.4↓B*
Pr_2O	0.1
Et_2O	0.08

* A = Negligible reaction with CF_2=$CFCF_3$, γ-rays, room temp.; B = formation of products with CF_2=$CFCF_3$.

'Krytox' fluid (Perfluoropolyether, DuPont) on Chromosorb P (column K). I.r. spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer using KBr plates. Proton and fluorine n.m.r. spectra were recorded on a Varian EM360L spectrometer operating at 60 and 56.4 MHz respectively and chemical shifts are quoted in p.p.m. relative to external tetramethylsilane and trichlorofluoromethane respectively; upfield shifts are positive. Mass spectra were recorded on a V.G. Micromass 12B spectrometer, fitted with a Pye 104 g.l.c. Hexafluoropropene (HFP) and other fluorinated alkenes were used without further purification while hydrocarbon substrates were purified by drying ($MgSO_4$) and distillation onto molecular sieves (4A). Peroxides were removed from ethers after which the latter were dried over sodium. Trimethyl borate was purified by the lithium chloride method to remove methanol.[16] Di-t-butyl peroxide (DTBP) was passed over an alumina column to remove traces of hydroperoxides. Gamma ray irradiations were performed in a purpose built shielded chamber with a cobalt-60 source (500 Curie original activity). Some of the compounds described in this paper did not respond satisfactorily to normal procedures for elemental analysis and gave values outside what would normally be regarded as satisfactory.

General Procedure for Radical Addition Reactions.—The reactions were carried out in sealed Pyrex Carius tubes (*ca.* 100 ml). The liquid reagents were added to the tube and degassed, then gaseous reagents were transferred to the tube *in vacuo*, using normal vacuum line techniques. The hydrocarbon substrate was usually used in a 2.5:1 excess over the fluoroalkene. The tube was sealed *in vacuo*, while frozen (liquid air). For gamma ray initiation, the tube was irradiated at a fixed distance and for a standard time, to give a total dose of *ca.* 10 Mrad, at a temperature of 18 °C. For thermal initiation using DTBP (at 1—5% w/w concentration) the tube was placed in a thermostatically controlled furnace at 140 °C for 18 h. The tube was opened while the contents were frozen (liquid air), gaseous components were transferred *in vacuo* to a trap cooled in liquid air, and the remaining liquid distilled to give excess hydrocarbon substrate and products.

Dimethyl ether. Dimethyl ether (9.8 g, 213 mmol) and hexafluoropropene (HFP) (13.8 g, 92 mmol) gave 2,2,3,4,4,4-hexafluorobutyl methyl ether (**4**)[7] (12.3 g, 68%).

Diethyl ether. Diethyl ether (14.5 g, 196 mmol) and HFP (10.8 g, 70 mmol) gave 2,2,3,4,4,4-hexafluoro-1-methylbutyl ethyl ether (**4b**)[5] (6.05 g, 38%) and bis-(2,2,3,4,4,4-hexafluoro-1-methylbutyl) ether (**5b**)[5] 5.84 g, 43%).

Dipropyl Ether. Dipropyl ether (14.6 g, 143 mmol) and HFP (9.5 g, 63 mmol) gave (*i*) *1-ethyl-2,2,3,4,4,4-hexafluorobutyl-propyl ether* (**4c**) (12%) (mixture of diasterioisomers), b.p. 46 °C (15 mmHg) (Found: C, 43.0; H, 6.0; F, 45.9. $C_9H_{14}F_6O$ requires C, 42.9; H, 5.6; F, 45.2%); δ_H 1.04 (6 H, m, Me), 1.67 (4 H, m, CH_2Me), 3.57, 4.00, and 5.03 (4 H, br m, CH_2O, CHO and CHF); δ_F 74.3 (3 F, m, CF_3), 117.5 and 120.2, 123.8 and 125.0 (2 F, br m, CF_2), and 211.7 (1 F, m, CFH); *m/z* 251 (M^+ − 1, 1%) and 101 (34), and 59 (100); (*ii*) bis(*1-ethyl-2,2,3,4,4,4-hexafluorobutyl)ether* (**5c**) (28%), b.p. 88—90 °C (15 mmHg) (Found: C, 36.3; H, 3.9; F, 56.1. $C_{12}H_{14}F_{12}O$ requires: C, 35.8; H, 3.5; F, 56.7%); δ_H 1.06 (3 H, m, Me), 1.79 (2 H, m, CH_2), 3.90 (1 H, m, CHO), and 5.01 (1 H, dm, *J* 46 Hz, CHF); δ_F 74.4 (3 F, m, CF_3), 122.0 (2 F, br, CF_2), and 212.1 (1 F, m, CFH); *m/z* 251 (M^+ − C_3HF_6, 13%) and 59 (100).

Dibutyl Ether. Dibutyl ether (15.7 g, 121 mmol) and HFP (11.8 g, 79 mmol) gave *2,2,3,4,4,4-hexafluoro-1-propylbutyl butyl ether* (**4d**) (16%) (mixture of diastereoisomers), b.p. 88—90 °C (25 mmHg) (Found: C, 46.8; H, 6.7; F, 44.6. $C_{11}H_{18}F_6O$ requires C, 47.1; H, 6.4; F, 40.7%); δ_H 0.67 (6 H, m, Me), 1.27 (8 H, m, CH_2), 3.32 (3 H, m, CH_2O, CHO), and 4.77 (1 H, dm, *J* 43 Hz, CHF); δ_F 76.2 (3 F, m, CF_3), 117.2 and 123.0 (AB, *J* 273 Hz) and 120.3 and 128.2 (each 2F, AB, *J* 273 Hz, CF_2), and 213.5 (1 F, m, CFH); *m/z* 237 (M^+ − C_3H_7, 1%), 129 (41), and 73 (100), (*ii*) *bis-(2,2,3,4,4,4-hexafluoro-1-propylbutyl) ether* (**5d**) (28%) (mixture of diastereoisomers), b.p. 120—130 °C (25 mmHg) (Found: C, 39.8; H, 4.5; F, 51.0. $C_{14}H_{18}F_{12}O$ requires C, 39.1; H, 4.2; F, 53.0%); δ_H 0.87 (3 H, m, Me), 1.52 (4 H, m, CH_2), 3.83 (1 H, m, CHO), and 4.87 (1 H, dm, *J* 44 Hz, CHF); δ_F 75.7 (3 F, m, CF_3), 121.0 (2 F, br, CF_2), and 212.7 (1 F, m, CFH); *m/z* 429 (M^+ − 1, 0.6%), 279 (17), and 73 (100), and (*iii*) 2,2,3,4,4,4-*hexafluoro-1-propylbutyl* [1-(1,1,2,3,3,3-*hexafluoro-1-propyl-propyl*)-2,2,3,4,4,4-*hexafluorobutyl*] *ether* (**6d**) (26%) (mixture of diastereoisomers) (Found: C, 38.3; H, 4.1; F, 59.4. $C_{17}H_{18}F_{18}O$ requires C, 35.2; H, 3.1; F, 59.0%); δ_H 1.03 (6 H, m, Me), 1.57, 2.10 (8 H, m, CH_2), 3.97 (1 H, m, CHO), and 4.87 (3 H, dm, *J* 42 Hz, CHF); δ_F 74.7 (3 F, m, CF_3), 120.0 (2 F, br, CF_2), and 211.2 (1 F, br, CFH); *m/z* 579 (M^+ − 1, 2%), 429 (37), 223 (34), and 73 (100).

Di-isopropyl ether. Di-isopropyl ether (9.8 g, 97 mmol) and HFP (5.8 g, 39 mmol) gave recovered starting materials (95%) with an unidentified product mixture (5%).

Methyl acetate. Methyl acetate (7.1 g, 96 mmol), HFP (5.4 g, 36 mmol), and DTBP (0.33 g) gave, after removal of starting materials, a product (4.2 g) which was separated by preparative g.l.c. to give (*i*) *2,3,3,-trifluoro-2-trifluoromethylpropyl acetate* (3%), b.p. 126 °C (760 mmHg) (Found: C, 32.4; H, 2.8; F, 51.6. $C_6H_6F_6O_2$ requires: C, 32.1; H, 2.7; F, 50.9%); $\nu_{max.}$ 1 760 cm^{-1} (C=O); δ_H 1.67 (3 H, s, Me), 4.20 (2 H, d, *J* 18 Hz, CH_2), 5.78 (1 H, td, *J* 53, 6 Hz, CH); δ_F 77.2 (3 F, m, CF_3), 135.7 (2 F, dm, *J* 52, 7 Hz, CF_2), and 191.2 (1 F, m, CF); *m/z* 225 (M^+ + 1, 0.3%) and 43 (100); (*ii*) *2,2,3,4,4,4-hexafluorobutyl acetate* (39%), b.p. 134 °C (760 mmHg) (Found: C, 34.3; H, 3.2; F, 49.7%). $\nu_{max.}$ 1 760 (C=O); δ_H 1.97 (3 H, s), 4.37 (2 H, m, CH_2), and 5.07 (1 H, dm, *J* 44 Hz, CH); δ_F 76.0 (3 F, m, CF_3), 117.3, 121.7 (2 F, AB, *J* 270 Hz, CF_2), and 213.8 (1 F, dm, *J* 44 Hz, CF); *m/z* 225 (M^+ + 1, 0.6%), 43 (100); (*iii*) *methyl 3,3,4,5,5,5-hexafluoropentanoate* (10%), b.p. 135 °C (760 mmHg) (Found: C, 32.2; H, 2.7; F, 50.8%), $\nu_{max.}$ 1 745 cm^{-1}; δ_H 2.77 (2 H, m, CH_2), 3.32 (3 H, s, Me), and 5.08 (1 H, dm, *J* 43 Hz, CH); δ_F 76.0 (3 F, m, CF_3), 109.3 (2 F, m, CF_2), and 213.8 (1 F, dm, *J* 43 Hz, CF); *m/z* 224 (M^+, 8%) and 193 (100); and (*iv*) 2,2,3,4,4,4-hexafluorobutan-1-ol (2%).[5]

Methyl formate. Methyl formate (6.6 g, 109 mmol), HFP (4.8 g, 32 mmol), and DTBP (0.46 g) gave, after removal of starting materials, a product (3.04 g) containing (*i*) methyl 2,2,3,4,4,4-

hexafluorobutanoate (5%), b.p. 116 °C (760 mmHg); δ_H 3.50 (3 H, s, Me) and 4.88 (1 H, dm, *J* 44 Hz, CH); δ_F 76.7 (3 F, m, CF_3), 118.0, 122.0 (2 F, AB, *J* 271 Hz, CF_2), and 216.0 (1 F, dm, *J* 44 Hz, CF); *m/z* 181 ($M^+ - O$, 1%), 59 (100), (*ii*) 2,2,3,4,4,4-*hexafluorobutyl formate* (11%), b.p. 119 °C (Siwoloboff) (Found: C, 29.0; H, 2.1; F, 54.2. $C_5H_4F_6O_2$ requires C, 28.6; H, 1.9; F, 54.3%); δ_H 4.59 (2 H, m, CH_2), 5.10 (1 H, dm, *J* 44 Hz, CHF), and 8.13 (1 H, s, HCO); δ_F 76.5 (3 F, m, CF_3), 117.4, 122.1 (2 F, AB, *J* 271 Hz, CF_2), and 208.5 (1 F, dm, *J* 42 Hz, CFH); *m/z* 209 ($M^+ - 1$, 1%), 69 (12), and 31 (100); and 2,2,3,4,4,4-hexafluorobutan-1-ol (21%).[5]

Dimethyl carbonate. Dimethyl carbonate (8.9 g, 98 mmol), HFP (7.5 g, 50 mmol), and DTBP (0.3 g) gave, after removal of starting materials, 2,2,3,4,4,4-*hexafluorobutyl methyl carbonate* (4.0 g, 55%), b.p. 146 °C (760 mmHg) (Found: C, 30.4; H, 2.8; F, 48.5. $C_6H_6F_6O_3$ requires C, 30.0; H, 2.5; F, 47.5%); δ_H 3.57 (3 H, s, Me), 4.30 (2 H, ddd, *J* 15, 10, 5 Hz, CH_2), and 4.92 (1 H, dm, *J* 44 Hz, CHF); δ_F 76.3 (3 F, m, CF_3), 119.3, 123.9 (2 F, AB, *J* 277 Hz, CF_2), and 215.8 (1 F, dm, *J* 43 Hz, CFH); *m/z* 241 ($M^+ + 1$, 1%), 45 (100).

Trimethyl borate.—(*a*) Trimethyl borate (16.5 g, 158 mmol) and HFP (10.3 g, 69 mmol) gave *tris*-(2,2,3,4,4,4-*hexafluorobutyl*) *borate* (**16**) (8.2 g, 65%), b.p. 62 °C (0.05 mmHg) (Found: C, 26.1; H, 1.8; B, 3.1; F, 61.5. $C_{12}H_9BF_{18}O_3$ requires C, 26.0; H, 1.6; B, 2.0; F, 61.7%); δ_H 3.97 (2 H, m, CH_2), 4.67 (1 H, dm, *J* 42 Hz, CHF); δ_F 75.5 (3 F, m, CF_3), 119.0, 123.0 (2 F, AB, *J* 263 Hz, CF_2), and 214.3 (1 F, dm, *J* 42 Hz, CFH); δ_{11_B} [$B(OMe)_3$ reference] −3.5 (br s); *m/z* 403 ($M^+ - C_3F_6H$, 26%), and 143 (100).

(*b*) Trimethyl borate (10.7 g, 105 mmol) and hexafluorocyclobutene (6.77 g, 42 mmol) gave *tris*-[(1,2,3,3,4,4-*hexafluorocyclobutyl*)*methyl*] *borate* (3.94 g, 49%), b.p. 72 °C (0.05 mmHg) (Found: C, 31.2; H, 1.5; B, 3.5; F, 58.0. $C_{15}H_9BF_{18}O_3$ requires C, 30.5; H, 1.5; B, 1.9; F, 58.0%); δ_H 4.13, 4.50 (2 H, s, CH_2), and 5.23 (1 H, dm, *J* 45 Hz, CHF); δ_F 118.8, 134.2 (AB, *J* 230 Hz, *cis*) and 121.1, 135.1 (AB, *J* 231 Hz, *trans*) (2 F, CF_2), 129.0, 131.1 (2 F, AB, *J* 231 Hz, CF_2, *cis* and *trans*), 180.5 (m, *trans*) and 198.2 (m, *cis*) (1 F, CF), 217.8 (dm, *J* 47 Hz, *trans*), and 219.7 (dm, *J* 47 Hz, *cis*) (1 F, CFH); *m/z* 427 ($M^+ - C_4F_6H$, 28%).

(*c*) Trimethyl borate (16.8 g, 161 mmol) and octafluorocyclopentene (16.5 g, 78 mmol) gave *tris*-[(1,2,3,3,4,4,5,5-*octafluorocyclopentyl*)*methyl*] *borate* (9.44 g, 49%), b.p. 133—136 °C (3 mmHg) (Found: B, 1.7; F, 61.7. $C_{18}H_9BF_{24}O_3$ requires B, 1.5; F, 61.6%); δ_H 4.39, 4.76 (2 H, s, CH_2), and 5.4 (1 H, br, CHF); δ_F 128.0 (6 F, br, CF_2), 180.6 (m, *trans*) and 195.1 (m, *cis*) (1 F, CF), 214.8 (dm, *J* 44 Hz, *trans*) and 226.5 (dm, *J* 46 Hz, *cis*) (1 F, CFH); *m/z* 527 ($M - C_5F_8H$, 2%).

(*d*) Trimethyl borate (9.2 g, 88 mmol) and decafluorocyclohexene (7.7 g, 29 mmol) gave *tris*-[(1,2,3,3,4,4,5,5,6,6-*decafluorocyclohexyl*)*methyl*] *borate* (6.2 g, 63%) b.p. 140 °C (3 mmHg) (Found: C, 28.5; H, 1.2; B, 2.5; F, 64.4. $C_{21}H_9BF_{30}O_3$ requires C, 28.3; H, 1.0; B, 1.2; F, 64.0%); δ_H 4.43 (2 H, br, CH_2) and 5.07 (1 H, br, CHF); δ_F 131.0 (8 F, br, CF_2), 187.2 (m, *trans*) and 194.2 (m, *cis*) (1 F, CF), 208.7 (dm, *J* 43 Hz, *trans*) and 231.3 (dm, *J* 43 Hz, *cis*) (1 F, CFH); *m/z* 624 (0.8%).

Tributyl borate. Tributyl borate (16.6 g, 72 mmol) and HFP (6.6 g, 44 mmol) gave an isomeric mixture of adducts of average composition [$B(OBu^t)_3$: C_3F_6 *ca.* 1.3], b.p. 65—67 °C (0.5 mmHg) (Found: C, 36.3; H, 3.6; M^+, 680. Calc. for $C_{21}H_{27}BF_{18}O_3$: C, 37.0; H, 3.9%; *M*, 680) and no HFP was recovered. Water (20 ml) was added to the adduct and the lower fluorocarbon layer was separated, dried ($MgSO_4$), and subjected to preparative g.l.c. (column K) to give (*i*) 1,1,1,2,3,3-*hexafluoroheptan-4-ol*, (**17**) (27%) (mixture of diasterioisomers); δ_H 0.9 (3 H, br, Me), 1.4 (4 H, br, 2xCH_2), 3.6, 4.1 (2 H, br, CHO, OH), and 5.1 (1 H, br m, CHF); δ_F 76.3 (3 F, m, CF_3), 111 to 134 (2 F, overlapping br, CF_2), 198.8, 200.4, 201.9, and 203.3 (1 F, m, CFH); *m/z* 186 (0.7%) and 73 (62), 55 (100) and (*ii*) 1,1,1,2,3,3-*hexafluoro*-4-(1,1,2,3,3,3-*hexafluoropropyl*)*heptan*-4-*ol* (**18**) (67%) (mixture of diastereoisomers) (Found: C, 32.7; H, 3.7; F, 59.1. $C_{10}H_{10}F_{12}O$ requires C, 32.1; H, 2.7; F, 60.9%); δ_H 1.00 (3 H, br, Me), 1.73 (4 H, br, 2xCH_2), 3.80 (1 H, br, OH), and 4.70 (2 H, br dm, *J* 44 Hz, CHF); δ_F 73.7 (3 F, m, CF_3), 123.0 (2 F, br, CF_2) and 210.7, 213.0 (1 F, m, CFH); *m/z* 223 ($M^+ - C_3F_6H$, 56%).

General Procedure for Decomposition of Di-t-Butyl Peroxide to Determine Acetone–t-Butyl Alcohol Ratios.—A mixture of DTBP (*ca.* 0.1 g) and substrate (10:1 molar excess) contained in a Pyrex Carius tube (*ca.* 7 ml) was degassed, sealed *in vacuo*, and heated at 120 °C for 8 h. The product was analysed by g.l.c. (diisodecyl phthalate (20%) on Chromosorb P, 85 °C) using a gas density balance detector and the amount of acetone and t-butyl alcohol determined from the area of their respective peaks. The acetone—t-butyl alcohol ratios determined for each substrate are listed in Table 1.

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