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SYNTHETIC UTILITY OF 3-(PERFLUORO-1,1-DIMETHYLBUTYL)-1-PROPENE. PART I. CONVERSION TO THE EPOXIDE AND TO ALCOHOLS

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SUMMARY

Various routes for the conversion of the title alkene to the corresponding epoxide and to alcohols were investigated. The new perfluoroalkyl epoxide $R_FCH_2\overbrace{CHCH_2O}$ and alcohols $R_FCH_2CH_2CH_2OH$, $R_FCH_2CH(OH)CH_3$, $R_FCH_2CH(OH)CH_2OCH_3$, and $R_FCH_2CHBrCH_2OH$, where $R_F = CF_3CF_2CF_2(CF_3)_2C-$, were obtained.

INTRODUCTION

Epoxides, alcohols, and carboxylic acids having long perfluoroalkyl substituents are important intermediates for the synthesis of fluorinated surfactants of unique properties. These compounds are usually derivatives of straight-chain perfluoroalkyl iodides which are synthesised by telomerisation of tetrafluoroethylene with perfluoroalkyl iodides C_1 - C_3 [1]. Free-radical addition of the telomer iodides to ethylene [2,3] and to vinyl acetate [2,4] gives, respectively, 2-(perfluoroalkyl)-1-iodoethanes and 2-(perfluoroalkyl)-1-iodoethyl acetates, and a number of methods for the conversion of these compounds to 2-(perfluoroalkyl)ethanols [5,6] and perfluoroalkyl epoxyethanes [4,7] have been described. Likewise, synthesis of 3-(perfluoroalkyl)propanols, propenols, and epoxypropanes by addition of perfluoroalkyl iodides to allyl alcohol or allyl acetate have also been reported [8,9,10].

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We wish to report another approach to compounds bearing a large perfluoroalkyl group, namely the tertiary perfluoro-1,1-dimethylbutyl group $CF_3CF_2CF_2(CF_3)_2C-$, using 3-(perfluoro-1,1-dimethylbutyl)-1-propene (1) as the starting material. This alkene was originally obtained by the Knunyants group [11] from perfluoro-2-methyl-2-pentene, i.e. the 'thermodynamic' dimer of hexafluoropropene, caesium fluoride, and allyl bromide in diglyme. Synthesis of alkene 1 has been later economised in our laboratory [12] by using, instead of caesium fluoride and diglyme, much less expensive potassium fluoride and dimethylformamide, and by the substitution of perfluoro-2-methyl-2-pentene with perfluoro-4-methyl-2-pentene, the easily available 'kinetic' dimer of hexafluoropropene. The use of phase-transfer catalysts allowed the rate of the reaction to be considerably increased and alkene 1 to be synthesised in over 90% yield and of high purity [13].

The present paper describes conversions of alkene 1 to the corresponding epoxide 2, to primary alcohols 8 and 10, and to secondary alcohols 6 and 9.

The general routes for the conversion of alkenes to alcohols are as follows [14]:

- acid catalysed hydration
- addition of hypohalous acids
- oxymercuration followed by treatment with sodium borohydride
- hydroboration followed by oxidation with peroxides
- epoxidation followed by hydrogenation of epoxides

Epoxides are usually obtained by direct oxidation of alkenes with peracids or by dehydrohalogenation of halohydrins formed by addition of hypohalous acids to alkenes [14]. Fluorine containing alkenes were also converted to epoxides via 1-acetoxy-2-halo derivatives which on treatment with a base produce epoxides [7,9,15].

All the above mentioned methods were applied or attempted to convert alkene 1 to the epoxide and to alcohols.

RESULTS AND DISCUSSION

Alkene 1 is totally immiscible with water and with mineral acids so, the attempted hydration with concentrated sulphuric acid and oxidation with aqueous hydrogen peroxide failed.

The attempted addition of sodium hypochlorite to alkene 1 in water or in an acetonitrile-water system in the presence of phase--transfer catalysts, methods which were successfully applied for the epoxidation of perfluoroalkenes [16], also resulted in total recovery of the unreacted 1.

Alkene 1 was successfully converted to 3-(perfluoro-1,1-dimethylbutyl)-1,2-epoxypropane (2) by oxidation with 3-chloroperbenzoic acid or perbenzoic acids. The reactions were conducted in chloroform which, as shown by the GLC, was contaminated with ca. 0.8% of carbon tetrachloride which resulted in a decreased yield of 2 by formation of an addition product, 4-(perfluoro-1,1-dimethylbutyl)-1,1,1,3-tetrachlorobutane (3), in ca. 13% yield.

$$CF_3CF_2CF_2C(CF_3)_2CH_2CH{=}CH_2 \xrightarrow{\text{peracid}} CF_3CF_2CF_2C(CF_3)_2CH_2\underset{\diagdown\,O\,\diagup}{CH{-}CH_2}$$

1 2 (30-50%)

The side reaction:

$$1 + CCl_4 \xrightarrow{\text{peracid}} CF_3CF_2CF_2C(CF_3)_2CH_2CHClCH_2CCl_3$$

3 (13%)

The direct oxidation of alkene 1, although it gives the expected epoxide 2, is very slow, employs expensive peracids, and the yields are not sufficient (30 - 50%). Therefore, we looked for other methods to convert alkene 1 to the required compounds.

Cambon and co-workers [7] reported conversion of perfluoroalkylethenes to the corresponding epoxides in a three-step process which involved simultaneous addition of bromine and the acetate ion, hydrolysis of the acetate ester, and dehydrobromination of the intermedia-

te bromohydrins. The addition of bromine and the acetate was performed with mercuric acetate and bromine in acetic acid.

The straight-forward adoption of the procedure described by Cambon [7], according to which the alkene was added dropwise to a mixture of other reactants, gave no satisfactory result when applied to alkene 1; an inseparable mixture of acetate esters 4 and 3-(perfluoro-1,1-dimethylbutyl)-1,2-dibromopropane (5) in a 44 : 56 ratio was obtained*. However, the reverse order of addition of the reactants, i.e. when bromine was slowly added to a stirred mixture of alkene 1 and mercuric acetate in acetic acid, gave the required acetate esters 4 in 91% yield and no trace of dibromide 5 was formed.

$$\underline{1} \xrightarrow{Hg(OAc)_2, Br_2, AcOH} \underset{\underline{4a}}{CF_3CF_2CF_2C(CF_3)_2CH_2CHBrCH_2OCOCH_3} + \underset{\underline{4b}}{CF_3CF_2CF_2C(CF_3)_2CH_2\underset{\displaystyle OCOCH_3}{\underset{|}{C}}HCH_2Br} + \underset{\underline{5}\ (0\text{-}56\%)}{CF_3CF_2CF_2C(CF_3)_2CH_2CHBrCH_2Br}$$

4a : 4b = 5 : 1 (total 44 - 91%)

There is much evidence that fast ionic addition of bromine to alkenes involve bromonium ion intermediates formed via alkene-bromine charge-transfer complexes [17,18,19]. A bromonium ion can react either with the bromide counter-ion to give a dibromo derivative or with any other nucleophile to form a product in which both bromine and a nucleophile add across the double bond of an alkene. This perfectly explains formation of a mixture of acetate esters 4 and the dibromide 5 when concentrations of the acetate and bromine in the reaction mixture are comparable, and the exclusive formation of 4

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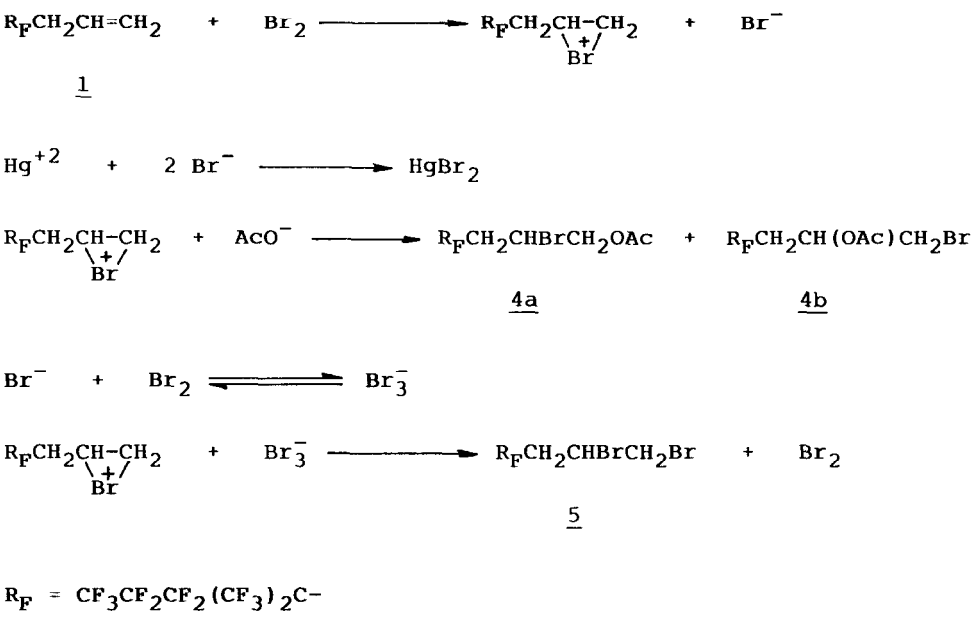
* *Compound 4 gave one GLC peak. The existence of the regioisomers 4a and 4b and their ratio was deduced after debromination to the GLC separable compounds 7a and 7b.*

when bromine is added at such a rate that it is immediately consumed and the acetate is in an excess. The reaction pathways leading to compounds 4 and 5 can be represented by the following equations:



R_F = $CF_3CF_2CF_2(CF_3)_2C-$

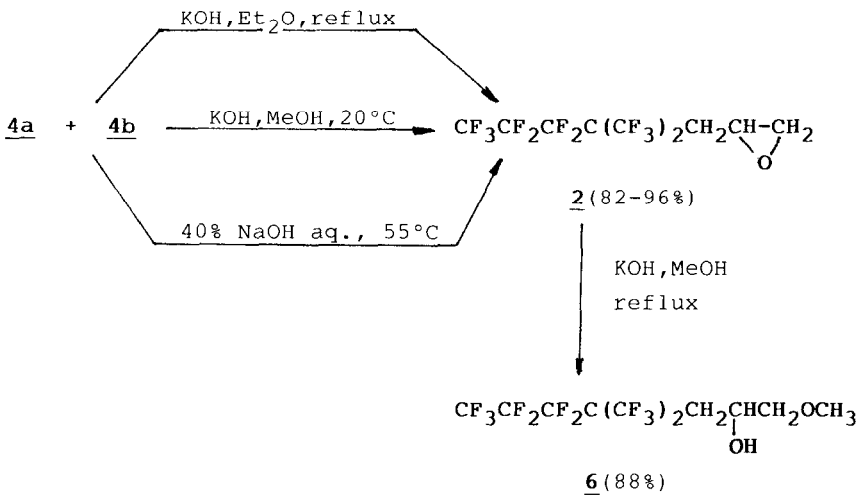
It has been checked in a separate experiment that bromine readily adds to alkene 1 in the absence of a mercuric salt to yield quantitatively dibromo derivative 5.

Alkenes having a perfluoroalkyl group bound directly to the vinylic carbon, like perfluoroalkylethenes [7] or 3,3,3-trifluoropropene [15], independently of the bromine concentration, reacted with bromine-acetic acid-mercuric acetate mixtures to give no dibromo derivatives. Therefore, for those reactions a different mechanism should be at work. Such alkenes have little tendency to form charge-transfer complexes but, due to their pronounced electron affinity, the initial step is, probably, nucleophilic attack by the acetate ion generated from mercuric acetate by interaction with bromine, as has been earlier postulated [7,15].

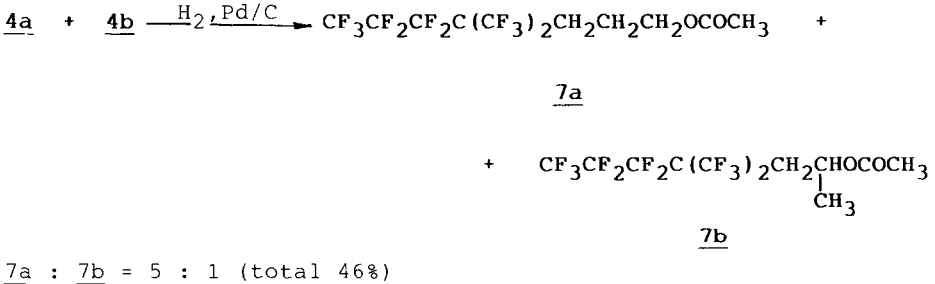
Acetates 4 showed different chemical properties as compared to similar compounds reported so far. A mixture of 4a and 4b on treatment with methanolic potassium hydroxide at 20°C immediately and quantitatively gave epoxide 2 which, when treated further with this reagent at the reflux temperature afforded 1-methoxy-3-(perfluoro-1,1-dimethylbutyl)-propan-2-ol (6). The reactions proceeded selectively and by the use of appropriate temperature either 2 or 6 were obtained in high yield and as the only products. This is in contrast to 3-(perfluoroalkyl)-2-halopropyl acetates previously reported [9] which under similar conditions undergo dehydrohalogenation to unsaturated derivatives. In the case of compounds 4 the lack of the dehydrobrominated products may be attributed to steric hindrances created by the tertiary perfluoroalkyl substituent which makes abstraction of a proton by the base difficult.

The reactions of acetates 4 either with aqueous sodium hydroxide or with solid potassium hydroxide, independently of the reaction temperature, stop at the stage of epoxide 2, thus providing an efficient method for its synthesis. For comparison, 2-(perfluoroalkyl)-2-bromoethyl acetates [7] under such conditions gave the corresponding bromohydrins.

Acetates 4 were found to be resistant to mineral acids: no hydrolysis occured after 24 hours refluxing with 10% sulphuric acid.

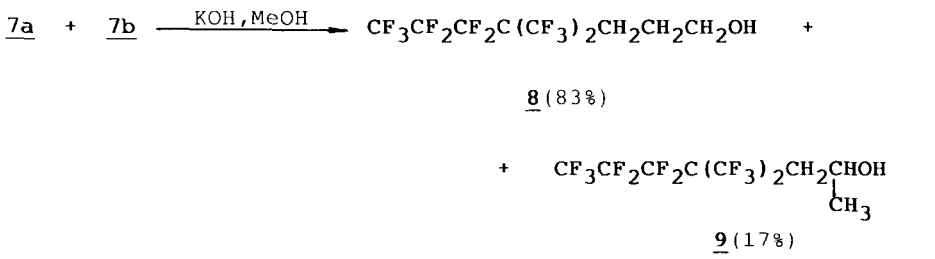


Catalytic hydrogenation of acetates 4 gave a mixture of debrominated esters, viz. 3-(perfluoro-1,1-dimethylbutyl)-propyl acetate (7a) and 1-methyl-2-(perfluoro-1,1-dimethylbutyl)-ethyl acetate (7b) in ca. 5 : 1 ratio (GLC estimate), albeit in low yield. No starting material was recovered which suggests that significant degradation of the perfluoroalkyl chain occurs.

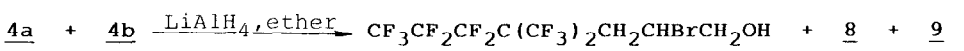


7a : 7b = 5 : 1 (total 46%)

Debrominated esters 7 when refluxed with methanolic potassium hydroxide gave a mixture of primary and secondary alcohols, i.e. 3-(perfluoro-1,1-dimethylbutyl)-propan-1-ol (8) and 3-(perfluoro-1,1-dimethylbutyl)-propan-2-ol (9).



Reduction of a mixture of acetates 4a and 4b with lithium aluminium hydride gave 3-(perfluoro-1,1-dimethylbutyl)-2-bromopropan-1-ol (10) as the main product together with alcohols 8 and 9. It is worth noting that the ratio of primary and secondary alcohols 8 and 9 (1 : 4) was opposite to the ratio of their precursors 4a and 4b and that no isomeric bromohydrin, deriving from 4b, was formed. This result indicates that the reduction of the terminal bromine in 4b is faster than of internal bromine in 4a.



$$\underline{4a} + \underline{4b} \xrightarrow{LiAlH_4,\ ether} CF_3CF_2CF_2C(CF_3)_2CH_2CHBrCH_2OH + \underline{8} + \underline{9}$$

10

10 : 8 : 9 = 11 : 1 : 4 (total 95%)

The secondary alcohol, 3-(perfluoro-1,1-dimethylbutyl)propan-2-ol (9), was obtained as the only product of the lithium aluminium hydride reduction of epoxide 2.

$$\underline{2} \xrightarrow{LiAlH_4,\ ether} CF_3CF_2CF_2C(CF_3)_2CH_2CH(CH_3)OH$$

9 (62%)

Preparation of primary alcohol 8 via esters 4 and 7 is inconvenient because it could not be separated by distillation from the accompanying secondary alcohol 9. Therefore, we undertook study on hydroboration of alkene 1.

Usual hydroboration procedures using borane or borane-dimethyl sulphide complex in tetrahydrofuran or diglyme resulted in less than 10% conversion. Alkene 1, however, readily reacted with borane--triethylamine complex [20] without a solvent at the reflux temperature. The reaction was practically complete in 15-20 minutes* and after one hour less then 2% of the unreacted 1 remained (GLC estimate). The best results were obtained when a 3 : 1.2 alkene-borane ratio was applied. Oxidation of the crude hydroboration product with 30% hydrogen peroxide in alkaline medium (NaOH) gave a mixture of four compounds: alcohols 8 and 9 and coupled alkanes, 1,6-bis(perfluoro-1,1-dimethylbutyl)-hexane (11) and probably 1,2-bis(perfluoro-1,1-dimethylbutyl)-2,3-dimethylbutane (12) (MS identification only), in the 35 : 47 : 14 : 4 ratio, respectively.

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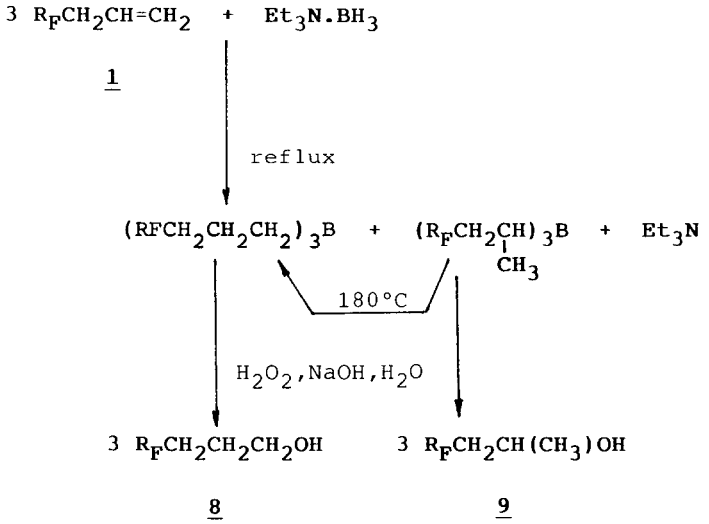
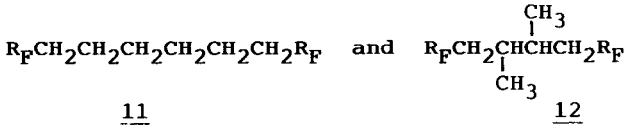
* *The reflux temperature dropped from the initial 117°C to 90°C due to the evolution of free triethylamine. Quantitative amounts of triethylamine could be distilled off.*

This result indicates that hydroboration of alkene 1 proceeds nonregioselectively, i.e. the boron attacks either the terminal or the internal vinylic carbon atom. However it is known that when nonterminal boranes are heated at temperatures ranging from 100 to 200°C, the boron moves toward the end of the chain [21]. Indeed, when the crude hydroboration mixture, prior to the oxidation, was heated in a sealed glass tube at 180°C for 16 hours, primary alcohol 8 and alkane 11 were obtained as the only products in a 4 : 1 ratio. Distillation gave the required alcohol 8 of 98% purity and in 68 - 72% yield.

The same results were obtained when the hydroboration was carried out in a stainless-steel autoclave at 170 - 180°C.



Side products:



R_F = $CF_3CF_2CF_2(CF_3)_2C-$

It has been checked that alkanes 11 and 12 were not present in the crude hydroboration mixtures, therefore, they must be formed during the oxidation step via a free-radical side process initiated by oxygen or hydroxyl radicals. This side reaction could not be avoided and causes a 15 - 20% decrease of the yield of alcohol 8, nevertheless, hydroboration of alkene 1 is the most practical way for its conversion to the primary alcohol.

The molecular compositions of compounds 2 - 11 were obtained from elemental analyses and mass spectra (Table 1). The structures of the hydrocarbon parts of these compounds were confirmed by the ^{1}H NMR spectra (Table 2). The ^{19}F NMR spectra were identical with those reported for a number of fluorohydrocarbons $CF_3CF_2CF_2C(CF_3)_2R$ [22].

EXPERIMENTAL

Boiling points were determined by distillation and are uncorrected. The NMR spectra were recorded with a Brucker MSL 300 spectrometer and the mass spectra with a Finnigan 8200 instrument. The GLC separations were performed with a Chrom 5 apparatus (Czechoslovakia) using a 3.5 m x 4 mm column for analytical work and a 3.5 m x 10 mm column for preparative separations, both columns packed with Chromosorb G coated with 3% Silicon Oil SE-52.

3-(Perfluoro-1,1-dimethylbutyl)-1-propene (1) was synthesized in this laboratory [13], other substrates were commercial laboratory reagents.

Epoxidation of alkene 1.

A solution of alkene 1 (18 g, 0.05 mole) and 85% 3-chloroperbenzoic acid (15 g, 0.08 mole) in chloroform (200 ml) was placed in a glass pressure tube and heated at 50°C for 7 days. After cooling to ambient temperature the precipitate of 3-chlorobenzoic acid was filtered off, the solution was concentrated to ca. 80 ml, filtered

TABLE 1

Physical properties and analyses of compounds 2 - 12.

R_F = $CF_3CF_2CF_2(CF_3)_2C$-

Compound	Molecular formula	B.P. °C(Torr)	Mass spectrum m/z(rel.intensity)	Analysis (%) found(calc.)
1	2	3	4	5
$R_FCH_2CH(O)CH_2$ 2	$C_9F_{13}H_5O$	159-161 28(0.7)	376(5)M^+, 307(8), 245(15), 207(54), 169(10), 145(24), 119(10), 69(99), 57(100)	C, 28.6(28.7) F, 65.7(65.7) H, 1.2(1.3)
$R_FCH_2CHClCH_2CCl_3$ 3	$C_{10}Cl_4F_{13}H_5$	56-58(0.2)	477(20)M^+-Cl, 441(100), 395(18), 381(38), 363(98), 343(45), 169(30), 145(30),119(20), 96(100), 69(80),	C, 23.3(23.4) F, 48.4(48.2) H, 1.1(1.0) Cl,27.8(27.5)
$R_FCH_2CHBrCH_2OCOCH_3$ and $R_FCH_2CH(OCOCH_3)CH_2Br$ 4a,4b	$C_{11}BrF_{13}H_8O_2$	56(0.3) 46(0.05)	440,438(9)M^+-AcOH, 419(3), 376(8), 361(11), 245(16), 195(24), 169(29), 145(63), 119(20), 69(100), 73(46)	C, 26.3(26.5) F, 49.4(49.5) H, 1.5(1.6) Br,16.0(16.0)

(continued overleaf)

TABLE 1 (cont.)

1	2	3	4	5
$R_FCH_2\underset{\underset{Br}{|}}{C}HCH_2Br$ 5	$C_9Br_2F_{13}H_5$	174-176 97-100(22) 54(0.6)	522,522(2),518M^+, 441(37), 439(45), 360(10), 359(15), 169(22), 145(68), 119(15), 69(100)	C, 21.0(20.8) F, 47.7(47.5) H, 1.0(1.0) Br,30.9(30.7)
$R_FCH_2\underset{\underset{OH}{|}}{C}HCH_2OCH_3$ 6	$C_{10}F_{13}H_9O_2$	185-186 40(0.1)	391(2)M^+-OH, 361(1), 169(2), 145(3), 119(3), 75(9), 71(12), 69(20), 57(9), 47(8), 45(100), 43(12), 31(28)	C, 27.3(27.4) F, 62.6(62.7) H, 1.9(1.8)
$R_FCH_2CH_2CH_2OCOCH_3$ and $R_FCH_2CH(OCOCH_3)CH_3$ 7a,7b	$C_{11}F_{13}H_9O_2$	42-44(0.5)	420(0.2)M^+, 377(0.6), 169(1), 119(1), 73(9), 69(12), 43(100), 42(4), 41(6), 31(14)	C, 31.6(31.5) F, 58.8(58.8) H, 1.8(1.9)
$R_FCH_2CH_2CH_2OH$ 8	$C_9F_{13}H_7O$	177-178 77(14) 70(10)	378(0.3)M^+, 377(0.6), 245(1), 69(7), 59(3), 41(9), 31(100)	C, 28.5(28.6) F, 65.2(65.3) H, 1.8(1.9)

$R_FCH_2\underset{\underset{OH}{|}}{C}HCH_3$ 9	$C_9F_{13}H_7O$	136	377(1)M^+-H, 363(16), 343(4), 169(4) 145(10), 119(6), 69(37), 45(100), 43(17)	C, 28.7(28.6) F, 65.3(65.3) H, 1.9(1.9)
$R_FCH_2\underset{\underset{Br}{|}}{C}HCH_2OH$ 10	$C_9F_{13}BrH_6O$	62-63(0.8)	377(8)M^+-Br, 376(6), 245(12), 207(5), 169(8), 145(15), 119(8), 69(73), 57(39), 45(15), 31(100)	C, 23.4(23.7) F, 54.1(54.1) H, 1.3(1.3) Br,17.5(17.5)
$R_F(CH_2)_6R_F$ 11	$C_{18}F_{26}H_{12}$	112(2)	722(0.1)M^+, 389(18), 361(6), 245(5), 169(10), 145(20), 119(5), 69(100), 56(12), 55(50)	C, 29.7(29.9) F, 69.1(69.0) H, 1.6(1.7)
$R_FCH_2\underset{\underset{CH_3CHCH_2R_F}{|}}{C}HCH_3$ 12	$C_{18}F_{26}H_{12}$		722(0.1)M^+, 389(4), 375(15), 245(3), 145(10), 119(2), 69(45), 55(100)	

TABLE 2

^{1}H NMR data for compounds 2 - 11.

R_F = $CF_3CF_2CF_2(CF_3)_2C$-

Compound	δ (ppm)*					Coupling const.
	H(a)	H(b)	H(c)	(CH_3)	(OH)	(Hz)
1	2	3	4	5	6	7
a b c $R_FCH_2CH(O)CH_2$	2.19(a)	3.21	2.55(c)			J(aa')=15.6
2**	2.58(a')		2.88(c')			J(cc')=4.6
a b c $R_FCH_2CHClCH_2CCl_3$	2.38(a)	4.70	2.83(c)			J(aa')=16.2
3**	2.61(a')		3.08(c')			J(cc')=15.1
a b c $R_FCH_2CHBrCH_2OCOCH_3$	2.87(a)	4.18	ca.4.4	2.07		J(aa')=17.0
4a**	2.97(a')					
a b c $R_FCH_2CH(OCOCH_3)CH_2Br$	ca.2.67	3.78	ca.4.45	2.04		J(aa')=16.9 J(cc')=11.0
4b**						
a b c $R_FCH_2CHBrCH_2Br$	2.87(a)	4.53	3.67(c)			J(aa')=17.3
5**	3.21(a')		3.37(c')			J(cc')=11.2
a b c $R_FCH_2CH(OH)CH_2OCH_3$	2.31(a)	4.28	3.26(c)	3.38	2.71	J(aa')=16.5
6**	2.38(a')		3.37(c')			J(cc')=9.3
a b c $R_FCH_2CH_2CH_2OCOCH_3$	2.25	1.97	4.07(t)	2.03		J(bc)=5.9
7a						

(continued)

TABLE 2 (cont.)

1	2	3	4	5	6	7
a b c $R_FCH_2CHCH_3$ $OCOCH_3$ 7b***	2.30(a) 2.68(a')	5.33	1.31(d)	2.00		J(aa')=16.6 J(bc)=6.3
a b c $R_FCH_2CH_2CH_2OH$ 8	2.30	1.85	3.61(t)		3.15	J(bc)=5.6
a b c $R_FCH_2CH(OH)CH_3$ 9***	2.32(a) 2.45(a')	4.32	1.31(d)		1.95	J(aa')=16.1 J(bc)=6.3
a b c $R_FCH_2CHBrCH_2OH$ 10**	2.86(a) 3.03(a')	4.44	3.75(c) 3.82(c')		2.50	J(aa')=17.4 J(cc')=12.4
a b c $R_FCH_2CH_2CH_2$ $R_FCH_2CH_2CH_2$ 11	2.15	1.65	1.38			

* In $CDCl_3$; centres of the signals related to internal TMS are quoted.

** ABXMN spin system.

*** $ABXM_3$ spin system

d - doublet, t - triplet

again, washed with saturated aqueous solution of sodium hydrogen carbonate followed by water and dried over anhydrous magnesium sulphite. The residue (16 g) obtained after removal of the solvent was distilled under atmospheric pressure to give 3-(perfluoro-1,1-dimethylbutyl)-1,2-epoxypropane (2) (**nc**) (9.4 g, yield 50%) as a colourless liquid with a delicate odour.

The distillation residue consisted mainly of 4-(perfluoro-1,1-dimethylbutyl)-1,1,1,3-tetrachlorobutane (3) (**nc**) (5 g, 13%). The analytical sample was obtained by preparative GLC.

In a similar run using perbenzoic acid (instead of 3-chloroperbenzoic acid), epoxide 2 was obtained in 30% yield together with large amount of a tar-like material.

Reaction of alkene 1 with mercuric acetate and bromine.

A. A mixture of alkene 1 (50.4 g, 0.14 mole), acetic acid (50 ml), and mercuric acetate (26.8 g, 0.084 mole) was cooled to 10 - 12°C, then a solution of bromine (22.4 g, 0.14 mole) in acetic acid (25 ml) was added dropwise, while stirring, at such a rate to keep the reaction temperature below 15°C (external cooling was applied). After addition of bromine the stirring was continued for half an hour at ambient temperature then, the reaction mixture was again cooled to 15°C, filtered, and the mercuric salts were washed with a small amount of cold ether. The filtrate was poured into iced water (ca. 100 ml), the organic layer was separated, dissolved in ether (120 ml) and the etheral solution was washed with aqueous potassium carbonate, water, and dried over anhydrous sodium sulphate. The residue obtained after removal of ether (66.5 g, yield 95%) consisted of 96% of a mixture of 3-(perfluoro-1,1-dimethylbutyl)-2-bromopropan-1-ol acetate (4a) and 3-(perfluoro-1,1-dimethylbutyl)-1-bromopropan-2-ol acetate (4b). Vacuum distillation gave a pure mixture of acetates 4 (**nc**) as a colourless liquid (compounds 4a and 4b appeared as one GLC peak).

B. Alkene 1 (7.2 g, 0.02 mole) was added dropwise at 5°C to a stirred mixture of acetic acid (13 ml), mercuric acetate (5.1 g, 0.016 mole),

and bromine (4.65 g, 0.03 mole). The reaction mixture was worked up as in A. The GLC of the crude product showed two well separated peaks in a 44 to 46 ratio. These compounds were identified by the comparative GLC analysis as acetates 4 (shorter RT) and 3-(perfluoro-1,1-dimethylbutyl)-1,2-dibromopropane (5), respectively. Distillation did not alter the ratio of products. Total yield 71% (7 g).

Bromination of alkene 1

Alkene 1 (7.2 g, 0.02 mole) was added dropwise at 0°C to a stirred solution of bromine (4.65 g, 0.03 mole) in acetic acid (13 ml). The reaction mixture was poured into iced water, the organic layer was separated, washed with aqueous sodium sulphite, dried, and distilled to give 3-perfluoro-1,1-dimethylbutyl)-1,2-dibromopropane (5) (nc) (9.2 g, 88%) as colourless liquid (GLC pure).

Conversion of acetates 4 to epoxide 2

A. A mixture of acetates 4 (7.5 g, 0.015 mole), powdered potassium hydroxide (3 g, 0.05 mole), and dry diethyl ether (30 ml) was refluxed for 12 hours. Water (25 ml) was added to the reaction mixture to dissolve inorganic salts, then the ether layer was separated and the water layer was extracted with ether (15 ml). The combined extracts were washed with water and dried over anhydrous sodium sulphate. The residue obtained after removal of the solvent was found to be a single compound (5.3 g, 94%) identified as 3-(perfluoro-1,1-dimethylbutyl)-1,2-epoxypropane (2). The product was purified by simple distillation.

B. A mixture of acetates 4 (2.5 g, 0.005 mole) was added to a solution of potassium hydroxide (0.6 g, 0.011 mole) in methanol (5 ml). A precipitate of potassium bromide and an oily bottom layer were immediately formed. A slight exothermic effect was observed. The reaction mixture was poured into water, the organic material was extracted with ether and identified as epoxide 2 (1.8 g, 96%).

C. Acetates 4 (7.5 g, 0.015 mole) and a 40% aqueous sodium hydroxide were vigorously stirred at 55°C for 48 hours. The reaction mixture was poured into iced water (30 ml), extracted with ether, the extract was washed with water and dried. Removal of the solvent gave epoxide 2 (4.6 g, 82%).

Preparation of 1-methoxy-3-(perfluoro-1,1-dimethylbutyl)-propan-2-ol 6

A. From epoxide 2.

A solution of epoxide 2 (5.6 g, 0.015 mole) and potassium hydroxide (1.1 g, 0.02 mole) in methanol (30 ml) was refluxed for 5 hours, then poured into water (30 ml). Organic material was extracted with ether, the extract was washed with water and dried over anhydrous magnesium sulphate. The viscous liquid obtained after evaporation of the solvent was identified as 1-methoxy-3-(perfluoro-1,1-dimethylbutyl)-propan-2-ol (6) (**nc**) (5.4 g, 88%). Pure compound 6 was obtained by vacuum distillation.

B. From acetates 4.

A solution of a mixture of acetates 4 (7.5 g, 0.015 mole) and potassium hydroxide (2 g, 0.036 mole) in methanol (30 ml) was refluxed for 5 hours and worked up as in **A** to give compound 6 as the only product (5.3 g, 87%).

Catalytic hydrogenation of acetates 4

Acetates 4 (7.5 g, 0.015 mole), triethylamine (3 g, 0.03 mole), a 10% palladium on carbon catalyst (0.9 g), and ethyl alcohol (30 ml) were placed in a Parr apparatus and hydrogenated at 20°C under initial hydrogen pressure 7 at. Fast pressure drop occurred and the reaction was practically completed during 30 minutes. The hydrogenation was continued for an additional 2 hours without any further pressure drop. The catalyst was filtered off, ethanol was evaporated, and the residue was mixed with water (40 ml) and extracted with ether.

The extract was washed with water and dried over anhydrous magnesium sulphate. Removal of the solvent gave a liquid (2.9 g, 46%) which was shown by the GLC to consist of two compounds in a 5 : 1 ratio. The elemental analysis of the mixture was consistent with that calculated for debrominated acetates 7. These compounds were separated by preparative GLC and identified as 3-(perfluoro-1,1-dimethylbutyl)-propyl acetate (7a) (**nc**) (major component, longer RT) and 1-methyl-2-(perfluoro-1,1-dimethylbutyl)-ethyl acetate (7b) (**nc**) (minor component, shorter RT).

The mixture of acetates 7 after refluxing with methanolic solution of potassium hydroxide was quantitatively converted to a 5 : 1 mixture of primary and secondary alcohols 8 and 9 (GLC identification by comparison with authentic samples).

Lithium aluminium hydride reduction of acetates 4

A solution of a mixture of acetates 4 (7.5 g, 0,015 mole) in dry ether (10 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (0.6 g, 0.016 mole) in 15 ml of ether at such a rate to keep the reaction mixture under slow reflux. The reflux was continued for an additional 2 hours then the reaction was quenched with water followed with 20% sulphuric acid. The ether layer was separated, washed with water and dried over anhydrous sodium sulphate. An oily liquid obtained after removal of the solvent (6.1 g, total yield 95%) was found by the GLC to consist of three components in an 1 : 4 : 11 ratio. The minor components were identified by comparative GLC analysis as alcohols 8 and 9, respectively. The main product (the longest RT) was isolated by vacuum distillation and identified as 3-(perfluoro-1,1-dimethylbutyl)-2-bromopropan-1-ol (10) (nc) (isolated yield 3.8 g, 55%).

Preparation of 3-(perfluoro-1,1-dimethylbutyl)-propan-2-ol (9)

A solution of epoxide 2 (5.4 g, 0.014 mole) in ether (10 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (0.3 g, 0,008 mole) in ether (10 ml) at such a rate to keep the reac-

tion mixture boiling gently. The reaction mixture was refluxed for an additional 3 hours and worked up as described above. Distillation gave 3-(perfluoro-1,1-dimethylbutyl)-propan-2-ol (9) (**nc**) as a colourless liquid (isolated yield 3.3 g, 63%).

Hydroboration of alkene 1.

A. A mixture of alkene 1 (20 g, 0.056 mole) and borane-triethylamine complex (2.6 g, 0.027 mole) was refluxed for 3 hours. After 20 min. the reflux temperature decreased from the initial 117°C to 90°C. The reaction mixture was cooled to ambient temperature, diluted with dry tetrahydrofuran (10 ml), and added dropwise with vigorous stirring to a solution of 30% hydrogen peroxide (15 ml), water (1 ml) and sodium hydroxide (1.2 g) cooled to -10°C. The oxidation proceeded exothermally and the rate of the addition was controlled to keep the temperature in the range -5 - 0°C. After completion of the addition the reaction mixture was stirred overnight at ambient temperature, then water was added (20 ml). The organic layer was separated, the water solution was extracted with ether (2 x 20 ml), the extract was combined with the main product and dried over anhydrous magnesium sulphate. The solvents (ether, THF) were distilled off (to 100°C) and the residue (17 g) was found by GLC to consist of five compounds. Comparison of the retention times with those of the authentic samples (obtained from other experiments) identified the first three and the fifth compound (in order of the increasing RT) as alkene 1 (0.9%), secondary alcohol 9 (34.8%), primary alcohol 8 (46.9%), and alkane 11, respectively. The fourth component (3.7%) was shown by the mass spectroscopy to be an isomeric fluoroalkane, most probably 12. Total GLC yield 81% (yield of alcohols 66.5%). The attempted separation of the alcohols by distillation gave fractions of ca. 80% purity, only.

B. Alkene 1 (40 g, 0.11 mole) and borane-triethylamine complex (5.4 g, 0.054 mole) were refluxed for 3 hours, then free triethylamine was distilled off (ca. 5 g) and the residue was heated, while stirring, at 180°C for 16 hours. The crude hydroboration product was diluted with tetrahydrofuran (20 ml) and oxidised as in **A** (30 ml 30%H_2O_2, 2 ml H_2O, 2.4 g NaOH) to give a mixture (38 g, total 91.5%) which was

shown by the GLC to contain alcohol 8 (80%) and alkane 11 (20%). No measurable amounts of isomeric products 9 and 12 were found. Distillation gave 3-(perfluoro-1,1-dimethylbutyl)-propan-1-ol (8) (**nc**) of 99% purity as a colourless, viscous liquid, (isolated yield 29.4 g, 70%) and 1,6-bis(perfluoro-1,1-dimethylbutyl)-hexane (11) (**nc**) as slightly yellow, viscous liquid (isolated yield, 6.5 g, 16%). An analytical, colourless sample of 11 was obtained by the preparative GLC.

C. Alkene 1 (100 g, 0.278 mole) and borane-triethylamine complex (13 g, 0.113 mole) were placed in a rocking stainless steel autoclave and heated at 170°C for 8 hours. The viscous reaction mixture was diluted with tetrahydrofuran (50 ml) and oxidised as in **A** (150 ml 30% H_2O_2, 10 ml H_2O, 7.7 g, NaOH). Distillation gave primary alcohol 8 (75 g, 71.5%) and alkane 11 (13 g, 13%) of 98% purity.

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