Polyfluorocycloalkenes. Part XII.[1] Reaction of Decafluorocyclohexene with Alkanediols in the Presence of Base

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Decafluorocyclohexene and sodium hydride in 2-acetoxyethanol and in propane-1,3-diol gave multicomponent mixtures comprising several partially fluorinated dioxa-heterocycles resulting from the base-assisted intramolecular reactions of the first formed 1- and 3-alkoxynonafluorocyclohexenes. With butane-1,4-diol only 1- and 3-(4-hydroxybutoxy)nonafluorocyclohexenes were formed; no cyclisation reactions were observed. These reactions emphasise some of the limitations of nucleophilic displacement reactions in the synthesis of heterocycles.

THE reactions of decafluorocyclohexene with alcohols under basic conditions yield both 1- and 3-alkoxynonafluorocyclohexenes.[2] Replacement of the alcohol by a diol (*e.g.* ethylene glycol[3]) gave a more complicated mixture [compounds (XIIa), (XVa), and (XIVa)] and some telomeric material. These results were explained in terms of a two-stage process involving addition of alkoxide anion to the electron-deficient double-bond followed by β-elimination of fluoride ion from the resulting carbanion to re-form the double bond. It was postulated that in the diol reaction the products isolated resulted from the intramolecular reactions of the (2-hydroxyethoxy)nonafluorocyclohexenes [(IIa), (IIIa)] or the anions [(IVa), (VIIIa)] derived therefrom, but there was no direct evidence for their presence in the reaction mixture.

The present work describes an attempt to prepare the primary products [(IIa), (IIIa)] of substitution, and a modified reaction scheme for the formation of the cyclised products is suggested. The limitations with respect to ring size of this intramolecular cyclisation are illustrated by the reaction of decafluorocyclohexene with propane-1,3- and butane-1,4-diols.

The failure to isolate the 2-hydroxyethyl ethers (IIa) and (IIIa) from the reaction of decafluorocyclohexene with solutions of bases in ethylene glycol with or without a co-solvent (*e.g.* tetrahydrofuran or dimethylformamide)

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[1] Part XI, J. A. Oliver, R. Stephens, J. C. Tatlow, and J. R. Taylor, submitted to *J. Fluorine Chem.*

[2] A. B. Clayton, J. Roylance, D. R. Sayers, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1965, 7358.

[3] G. Camaggi and R. Stephens, *Tetrahedron*, 1966, **22**, 1189.

under diverse conditions prompted the use of a blocking-group procedure. A half-ester of ethylene glycol was chosen; 2-acetoxyethanol reacted with decafluorocyclohexene in the presence of sodium hydride to give compounds (XIIa) (37% by weight) and (XVa) (2%), ethylene acetate (7%), and compounds (IIIb) (5%), (IIb) (38%), (XIVa) (1%), (VIa) (2%), and (Va) (8%), which except for (XIVa) (tentatively identified by retention time) were separated by g.l.c. We were unable to control the reaction so that only compounds (IIb) and (IIIb) were produced.

1-(2-Acetoxyethoxy)nonafluorocyclohexene (IIb) was resistant to hydrolysis by mineral acid. Both compound (IIb) and 3-(2-acetoxyethoxy)nonafluorocyclohexene (IIIb) reacted with hot aqueous potassium hydroxide; the latter gave (XVa), (XIVa), and an unidentified compound [(IIIa)?], whereas the former was converted partly into (XIIa).

A reaction pathway (see Scheme) leading to these ethers is based on an addition–elimination sequence of the type applicable to simple alcohol–perfluorocycloalkene reactions.[2] Nucleophilic attack by the acetoxyethoxide ion on the double bond of decafluorocyclohexene produces the anion (I), which can eliminate fluoride ion from C-1 (inwards) and/or C-3 (outwards), the former being favoured, to give the 2-acetoxyethyl ethers (IIb) and (IIIb), respectively. These are the primary products; the others are derived from the reactions of the anions (VIIIa) and (IVa) produced by saponification of (IIIb) and (IIb). In the present reaction, however, these anions, as well as yielding (XIIa), (XVa), and (XIVa) by intramolecular reactions, react further with decafluorocyclohexene to give the 1,2-bis(nonafluorocyclohexenyloxy)ethanes (VIa) and (Va) by 'outwards' and 'inwards' eliminations of fluoride ion from the intermediate carbanion. Compound (VIIa) was not detected; it would be the minor product from attack by the anion (VIIIa), itself derived from a minor component, on decafluorocyclohexene. Treatment of decafluorocyclohexene with an excess of ethylene glycol should prevent the formation of the diethers, but if they were formed further reaction would give rise to telomeric material, as was isolated.[3]

Under basic conditions the acetate (IIb) is hydrolysed to the anion (IVa), which could cyclise to give the carbanions (IX) and (X). The sole observed product of this reaction is (XIIa); therefore the anion (X) is not formed, since loss of fluoride ion would take place readily. By analogy with the reaction[2] of 1-methoxynonafluorocyclohexene with sodium methoxide in methanol, attack at C-2 in (IVa) would be expected: however factors leading to attack at this position are presumably overridden by the highly favoured formation of the five-membered ring.[4]

Recently, Gambaretto *et al.*[5] have described this preference for the formation of five-membered rings in the reaction of 1-chlorononafluorocyclohexene with alkaline ethylene glycol: 6-chloro-12,12,13,13,14,14-hexafluoro-1,4,8,11-tetraoxadispiro[4.1.4.3]tetradecane was produced. Also 1-(2-hydroxyethoxy)heptafluorocyclohexa-1,4-diene, isolated from the reaction of octafluorocyclohexa-1,4-diene with alkaline ethylene glycol, cyclised exclusively to spiro-dioxolan-type compounds on treatment with base.[6]

A small amount of 3-(2-acetoxyethoxy)nonafluorocyclohexene was saponified with aqueous potassium hydroxide. Isolation of the three products proved to be impracticable but the presence of compounds (XVa) and (XIVa) and the absence of (XIIa), (XIIIa), and unchanged acetate (IIIb) was confirmed by g.l.c. (by enrichment techniques); the third product was thought to be (IIIa). The anion (VIIIa) is an excellent example of a system which could undergo an intramolecular allylic S_N-type displacement reaction. Although the direct displacement of isolated allylic halogen atoms by alkoxide ions is well known,[7] there appears to be no example of such a displacement from a highly fluorinated alkene. An early claim[8] for this type of reaction was challenged recently; the products arising from the reactions of 1*H*,2*H*-tetrafluorocyclobutene, 1*H*,2*H*-hexafluorocyclopentene, and 1*H*,2*H*-octafluorocyclohexene with solutions of sodium methoxide were all accounted for by addition–elimination processes.[9] The absence of (XIIa) in the reaction mixture provides further evidence that the direct displacement of allylic fluorine atoms in highly fluorinated systems is unlikely. Thus these results suggest an alternative explanation of those obtained by Camaggi and Stephens.[3]

The chance of isolating the primary substitution products from the reaction of decafluorocyclohexene with diols would be expected to increase if the subsequent cyclisation reactions are less favoured. The reactions of decafluorocyclohexene with propane-1,3-diol and butane-1,4-diol illustrate this.

Decafluorocyclohexene reacted with potassium hydroxide in a large excess of propane-1,3-diol to give compounds (IIIc) (14% by weight), (XIIb) (1%), (IIc) (25%), (XIIIb) (17%), (XVb) (11%), (XIVb) (22%), (VIb) and (VIIb) (4%), and (Vb) (6%), which were separated by preparative g.l.c., and a sticky involatile liquid.

Compounds (XIIIb), (XVb), and (XIVb) each had the same molecular weight and were characterised by i.r. and n.m.r. spectroscopy. Both compounds (XVb) and (XIVb) were isomerised to (XIIIb) when treated with potassium fluoride in dimethylformamide.[3,10] Only one (Vb) of the three bis(nonafluorocyclohexenyloxy)propanes was isolated; the other two [(VIb), (VIIb)] formed an inseparable mixture. These diethers were

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[4] E. L. Eliel, 'Stereochemistry of Carbon Compounds,' McGraw-Hill, New York, 1962, p. 198.

[5] G. Gambaretto, M. Napoli, and S. Gliozzi, *Ann. Chim. (Italy)*, 1969, **59**, 702.

[6] M. C. V. Cane and R. G. Plevey, unpublished work.

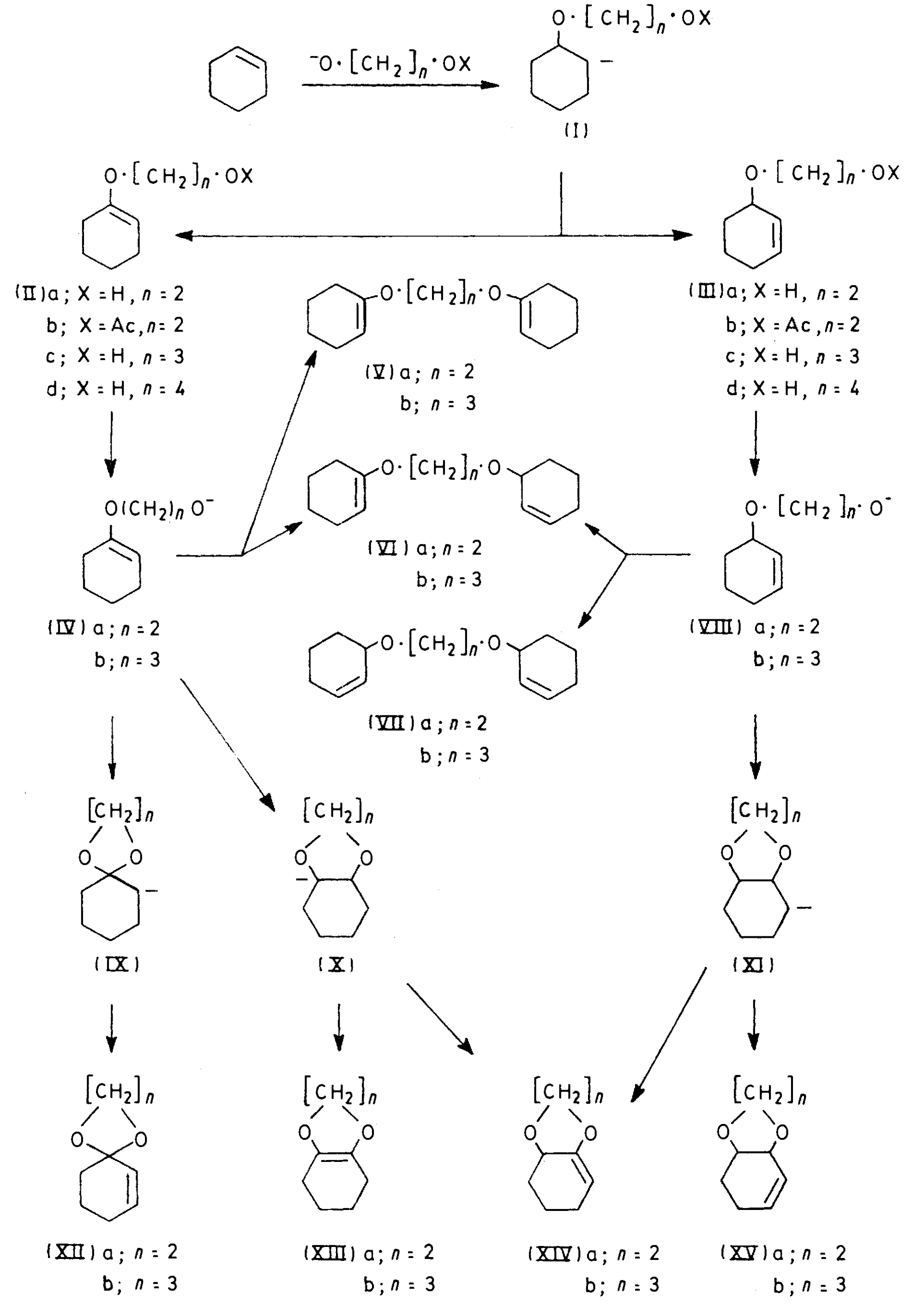
[7] R. H. DeWolfe and W. G. Young, *Chem. Rev.*, 1956, **56**, 836.

[8] J. R. Lacher, J. D. Park, and L. H. Wilson, *J. Org. Chem.*, 1963, **28**, 1008.

[9] A. B. Clayton, D. Collins, R. Stephens, and J. C. Tatlow, *J. Chem. Soc. (C)*, 1971, 1177.

[10] W. J. Feast and R. Stephens, *J. Chem. Soc.*, 1965, 3502.

identified by i.r. and n.m.r. spectroscopy and were the major products of a reaction in which the alkaline solution of propane-1,3-diol was treated with a large excess of decafluorocyclohexene.



SCHEME All unmarked bonds to fluorine

With a limited amount of base, just two products, (IIIc) and (IIc), were formed, in the ratio 3 : 2. They were separated by g.l.c. and identified by i.r. and n.m.r. spectroscopy. Compound (IIc) in the presence of base gave a mixture of three compounds, separated by g.l.c. and identified as (XIIIb), (XIVb), and (tentatively) (XIIb). The absence of compound (XVb) was confirmed by g.l.c. (by enrichment techniques). In a similar reaction (IIIc) gave a mixture of three components [(IIIc), (XVb), and (XIVb)].

The reaction between decafluorocyclohexene and propane-1,3-diol may be explained in an analogous way to the ethylene glycol reaction (Scheme). However in the former reaction the two primary substitution products [(IIIc), (IIc)] can be isolated. The cyclisation of (IIc) *via* the anion (IVb) resulting in seven-membered ring formation [(XIIIb), (XIVb)] rather than giving the spiro[6.6]-compound (XIIb) was unexpected. However it has been shown that further substitution of alkoxynonafluorocyclohexenes with alkoxides occurs at C-2,[2] and so the slightly longer side-chain in the anion (IVb) in comparison with (IVa) must permit greater freedom for the alkoxide anion to attack intramolecularly at the position dictated by the substituents on the double bond. Also there seems to be slightly less steric crowding in the intermediates resulting in (XIIIb) and (XIVb) than in that leading to (XIIb). The ease of ring formation is of less significance in this reaction.

Finally, the reaction of decafluorocyclohexene with butane-1,4-diol gave 1-(4-hydroxybutoxy)nonafluorocyclohexene (IId) and 3-(4-hydroxybutoxy)nonafluorocyclohexene (IIId) in good yield in the ratio 5 : 4. The reaction was performed under conditions which would prevent the formation of any bis(nonafluorocyclohexenyloxy)butanes. Compounds (IIId) and (IId) did not undergo any cyclisation reactions under basic conditions, in accord with the known difficulties associated with the formation of medium-sized ring compounds.[4]

EXPERIMENTAL

For preparative g.l.c. five columns were used: unit 1, silicone gum–Celite (1 : 7) (910 × 0.6 cm); unit 2, Carbowax (mol. wt. 6 000)–Chromosorb P (1 : 5) (910 × 0.6 cm); unit 3, polyethylene glycol adipate–Celite (1 : 4) (1 200 × 0.6 cm) (all on a Pye series 104 or 105 instrument); unit 4, silicone gum–Celite (1 : 7) (488 × 3.5 cm); unit 5, Carbowax (mol. wt. 1 000)–Celite (1 : 5) (488 × 3.5 cm). For analytical g.l.c. a Perkin-Elmer F11 chromatograph fitted with a Golay capillary column containing Ucon oil LB-550-X (10 000 × 0.025 cm) (unit 6) was also used.

I.r. spectra were measured with a Perkin-Elmer 257 grating spectrometer. N.m.r. spectra (^{1}H and ^{19}F) were measured with a Perkin-Elmer R10 spectrometer; unless stated otherwise samples were dissolved in carbon tetrachloride, with tetramethylsilane or trichlorofluoromethane as internal standard. The ^{19}F n.m.r. data of compounds (IIb—d), (IIIb—d), (Va and b), (VIa and b), (XIIa and b), and (XIIIa and b) are listed in Supplementary Publication No. SUP 21622 (3 pp.).* Mass spectra were measured with an A.E.I. MS9 spectrometer.

Reaction of Decafluorocyclohexene with 2-*Acetoxyethanol.*—2-Acetoxyethanol (9.4 g, 0.09 mol) and a suspension of sodium hydride (2.2 g, 0.09 mol) in decafluorocyclohexene (20.0 g, 0.08 mol) were stirred together for 1 h, water (70 cm^3) was added, and the lower, organic layer was separated, washed with water, dried, and distilled to give decafluorocyclohexene (1.8 g), and a mixture (13.4 g), b.p.

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(VIa) (0.09 g), tentatively identified by spectroscopy, $\nu_{max.}$ 1 740 (CF=CF) and 1 708 cm^{-1} (CF=C), τ 5.6 (s, O·CH$_2$·CH$_2$·O), and (iie) *bis*-1,2-(*nonafluorocyclohex*-1-*enyloxy*)-*ethane* (Va) (0.36 g) (Found: C, 30.5; H, 0.9%; M^+, 546. $C_{14}H_4F_{18}O_2$ requires C, 30.8; H, 0.7%; M, 546), $\nu_{max.}$ 1 708 cm^{-1} (CF=C), τ 5.4 (t, O·CH$_2$·CH$_2$·O, J_{HF} 1.5 Hz). Sub-fraction (iia) was separated further (unit 1, 127 °C, N$_2$ at 8.2 l h^{-1}) to give 1,6,7,8,9,9,10,10-octafluoro-2,5-dioxabicyclo[4.4.0]dec-7-ene (XVa) (trace) and ethylene acetate (0.05 g). Sub-fraction (iib) (0.47 g) was washed with water and separated (unit 1, 127 °C, N$_2$ at 8.2 l h^{-1}) to give compound (XVa) (0.038 g) and 3-(2-*acetoxyethoxy*)-*nonafluorocyclohexene* (IIIb) (0.037 g), M^+ (346) not detected, m/e 286.002 (M − HOAc), $\nu_{max.}$ 1 750 cm^{-1} (acetate C=O, CF=CF), τ 7.93 (3 H, s, OAc) and 5.72 (4 H, m, O·CH$_2$·CH$_2$·O). Compounds (XIIa) and (XVa) were recognised by their i.r. spectra.[3,11] The presence of 1,7,8,8,9,9,10,10-octafluoro-2,5-dioxabicyclo[4.4.0]dec-6-ene (XIVa) was inferred from g.l.c. enrichment studies.

Reaction of 1-(2-*Acetoxyethoxy*)*nonafluorocyclohexene* (IIb) *with Aqueous Potassium Hydroxide.*—Compound (IIb) (1.0 g) was stirred with potassium hydroxide (0.6 g) in water (1.0 cm^3) at 85 °C for 84 h. Water (5 cm^3) was added and the organic layer (0.60 g) run off and separated by g.l.c. (unit 2, 150 °C, N$_2$ at 8.6 l h^{-1}) to give the dioxolan (XIIa) (0.22 g) and the acetate (IIb) (0.11 g), identified by i.r. spectra.

Reaction of 3-(2-*Acetoxyethoxy*)*nonafluorocyclohexene* (IIIb) *with Aqueous Potassium Hydroxide.*—Compound (IIIb) (0.13 g) was stirred with potassium hydroxide (0.3 g) in water (0.6 cm^3) at 90 °C for 44 h. Water (2 cm^3) was added and the mixture extracted with ether (0.5 cm^3). The extract was concentrated by distillation and examined by analytical g.l.c. (unit 6, 130 °C, N$_2$ 2 kg cm^{-2}). Two of three products indicated in the ethereal solution were identified as compounds (XVa) and (XIVa) but the other was not identified; it was not (XIIa) or (IIIb).

Reaction of Decafluorocyclohexene with Propane-1,3-*diol.*—(*a*) Decafluorocyclohexene (22 g, 0.082 mol), sodium hydride (1.0 g, 0.42 mol), and propane-1,3-diol (40 cm^3) were stirred together for 1 h, then poured into water (70 cm^3), and the organic layer (18.0 g) was separated, dried, and distilled to give decafluorocyclohexene (7.1 g) and a mixture (9.6 g), b.p. 70—80° at 0.5 mmHg. The mixture (0.65 g) was separated by g.l.c. (unit 1, 128 °C, N$_2$ at 5.6 l h^{-1}) to give (i) 3-(3-*hydroxypropoxy*)*nonafluorocyclohexene* (IIIc) (0.12 g), b.p. 188° (Found: C, 34.3; H, 2.3. $C_9H_7F_9O_2$ requires C, 34.0; H, 2.2%), M^+ (318) not detected, m/e 300.013 (M − H$_2$O), $\nu_{max.}$ 1 740 (CF=CF) and 3 350 cm^{-1} (OH), τ 8.16 (2 H, quintet, C·CH$_2$·C, $J_{H,H}$ 6 Hz), 6.90 (1 H, s, OH), 6.39 (2 H, t, O·CH$_2$, $J_{H,H}$ 6 Hz), and 5.92 (2 H, t, O·CH$_2$, $J_{H,H}$ 6 Hz); and (ii) 1-(3-*hydroxypropoxy*)*nonafluorocyclohexene* (IIc) (0.17 g), b.p. 194° (Found: C, 34.1; H, 2.4%;

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heated under reflux for 16 h, then poured into water (70 cm^3), and the organic layer was separated, dried, and distilled to give a liquid mixture (6.0 g), b.p. 90—125° at 15 mmHg, and a viscous yellow liquid (3.8 g), b.p. 140—160° at 0.5 mmHg, $\nu_{max.}$ 1 650—1 750 cm^{-1}, probably containing telomers. The liquid mixture (5.0 g) was separated by g.l.c. (unit 3, 150 °C, N_2 at 4 l h^{-1}) to give (i) a mixture (0.57 g), (ii) a mixture (0.82 g), and (iii) 1,8,9,9,10,10,11,11-*octafluoro*-2,6-*dioxabicyclo*-[5.4.0]*undec*-7-*ene* (XIVb) (0.73 g), b.p. 219° (Found: C, 35.8; H, 2.2%; M^+, 298. $C_9H_6F_8O_2$ requires C, 36.2; H, 2.1%; *M*, 298), $\nu_{max.}$ 1 700 cm^{-1} [CF=C(OR)], τ 7.9 (2 H, m, $CH_2{\cdot}CH_2{\cdot}CH_2$) and 5.7 (4 H, m, $O{\cdot}CH_2$), ^{19}F n.m.r. ϕ − 115.1 and − 119.0 (AB system, *J* 282 Hz), −131.2 and −134.5 (AB_2 system, *J* 268 Hz), −121.7(m) and −157.3 (relative intensities 2 : 4 : 1 : 1) [in $(CD_3)_2CO$ −116.0(m), −120.9(m), −131.9(m) and −159.2(m) (2 : 1 : 4 : 1)]. Fraction (i) (0.55 g) was separated further (unit 3, 124 °C, N_2 at 4 l h^{-1}) to give (ia) a mixture (0.15 g) of mainly 1-(*nonafluorocyclohex*-1-*enyloxy*)-3-(*nonafluorocyclohex*-2-*enyloxy*)*propane* (VIIb), identified tentatively by spectroscopy, $\nu_{max.}$ 1 745 (CF=CF) and 1 700 cm^{-1} [CF=C(OR)], τ 7.83 (2 H, quintet, $CH_2{\cdot}CH_2{\cdot}CH_2$, $J_{H,H}$ 6 Hz), 5.75 (2 H, t, $O{\cdot}CH_2$, $J_{H.H}$ 6 Hz), and 5.50 (2 H, td, $O{\cdot}CH_2$, $J_{H.H}$ 6, J_{HF} 2.5 Hz), contaminated with 1,3-bis(nonafluorocyclohex-2-enyloxy)propane (VIb) (i.r. and ^{1}H and ^{19}F n.m.r. signals consistent with this structure were observed); and (ib) 1,3-*bis*(*nonafluorocyclohex*-1-*enyloxy*)*propane* (Vb) (0.22 g), b.p. 232° (Found: C, 31.8; H, 1.2. $C_{15}H_6F_{18}O_2$ requires C, 32.3; H, 1.1%), M^+ (560) not detected, *m/e* 301 ($M - C_6F_9O$), τ 7.77 (2 H, quintet, $CH_2{\cdot}CH_2{\cdot}CH_2$, $J_{H.H}$ 6 Hz) and 5.85 (4 H, td, $O{\cdot}CH_2$, $J_{H.H}$ 6, $J_{H.F}$ 3 Hz). Fraction (ii) (0.45 g) was separated further (unit 1, 100 °C, N_2 at 2 l h^{-1}) to give (iia) 8,8,9,9,10,10,11,11-*octafluoro*-2,6-*dioxabicyclo*[5.4.0]*undec*-1(7)-*ene* (XIIIb) (0.14 g), b.p. 203° (Found: C, 36.4; H, 2.0%; M^+, 298. $C_9H_6F_8O_2$ requires C, 36.2; H, 2.1%; *M*, 298), $\nu_{max.}$ 1 670 cm^{-1} [C(OR)=C(OR)], τ 5.67 (4 H, t, $O{\cdot}CH_2$) and 7.76 (2 H, quintet, CH_2, $J_{H.H}$ 6 Hz); and (iib) 1,7,8,9,10,10,11,11-*octafluoro*-2,6-*dioxabicyclo*[5.4.0]*undec*-8-*ene* (XVb) (0.14 g) (Found: C, 36.2; H, 2.2%; M^+, 298. $C_9H_6F_8O_2$ requires C, 36.2; H, 2.1%; *M*, 298), $\nu_{max.}$ 1 745 cm^{-1} (CF=CF), τ 8.00 (2 H, s, $C{\cdot}CH_2{\cdot}C$) and 5.76 (4 H, s, $O{\cdot}CH_2$), ^{19}F n.m.r. ϕ − 116.1 and −123.3 (AB system, *J* 282 Hz), −128.0 and −136.5 (AB, *J* 262 Hz), −127.6(m), −132.6(m), −139.3 (m), and −159.2(m) (relative intensities 2 : 2 : 1 : 1 : 1 : 1).

Since compounds (IIIc) and (IIc) were not recovered from g.l.c. unit 3 an alternative separation (unit 4, 120 °C, N_2 at 12 l h^{-1}) of the liquid mixture (2.7 g) gave (iv) a mixture further separated (unit 1, 120 °C, N_2 at 4 l h^{-1}) to give (IIIc) (0.12 g), (XIIb) (trace—see later), and (IIc) (0.17 g) identified by i.r. spectroscopy; and (v) a mixture (1.98 g) whose components had g.l.c. retention times coincident with those of compounds (XIIIb), (XVb), (XIVb), (VIb), (VIIb), and (Vb).

(*c*) *With an excess of decafluorocyclohexene.* Decafluorocyclohexene (30 g, 0.114 mol), powdered potassium hydroxide (1.5 g, 0.027 mol), and propane-1,3-diol (1 g, 0.013 mol) were heated under reflux for 3 h, then poured into water (60 cm^3), and the organic layer was separated, dried, and distilled to give decafluorocyclohexene (23.5 g); a mixture (3.7 g), part (3.0 g) of which was separated (unit 3, 128 °C, N_2 at 4 l h^{-1}) to give compounds (VIb) and (VIIb) (0.5 g) and compound (Vb) (1.0 g), identified by i.r. spectroscopy; and a viscous liquid (0.8 g), b.p. 140—200° at 13 mmHg (not investigated).

Cyclisation of Compound (IIc).—Compound (IIc) (0.8 g), sodium hydride (0.2 g), and dimethylformamide (4 cm^3) were stirred for 24 h at 21 °C, poured into water (15 cm^3), and extracted with ether. The extracts were washed with water and dried ($MgSO_4$), and the ether was removed by distillation. Distillation of the residue *in vacuo* gave a liquid (0.55 g) which was separated by g.l.c. (unit 1, 130 °C, N_2 at 5.6 l h^{-1}) to give (i) dimethylformamide (0.02 g); (ii) 7,8,9,9,10,10,11,11-*octafluoro*-1,5-*dioxaspiro*[5.5]*undec*-7-*ene* (XIIb) (0.03 g), $\nu_{max.}$ 1 740 cm^{-1} (CF=CF), τ 5.80 (4 H, m, $O{\cdot}CH_2$) and 8.08 (2 H, m, $C{\cdot}CH_2{\cdot}C$); (iii) 8,8,9,9,10,10,11,11-octafluoro-2,6-dioxabicyclo[5.4.0]undec-1(7)-ene (XIIIb) (0.05 g); and (iv) 1,8,9,9,10,10,11,11-octafluoro-2,6-dioxabicyclo[5.4.0]undec-7-ene (XIVb) (0.16 g).

Cyclisation of Compound (IIIc).—Compound (IIIc) (0.5 g), sodium hydride (0.2 g), and dimethylformamide (4 cm^3) were stirred for 24 h at 21 °C. The mixture was worked up as in previous experiments to give (i) dimethylformamide (0.01 g); (ii) (IIIc) (0.06 g); (iii) 1,7,8,9,10,10,11,11-octafluoro-2,6-dioxabicyclo[5.4.0]undec-8-ene (XVb) (0.03 g); and (iv) 1,8,9,9,10,10,11,11-octafluoro-2,6-dioxabicyclo-[5.4.0]undec-7-ene (XIVb) (0.03 g).

Isomerisation of Compound (XIVb).—Compound (XIVb) (0.7 g), anhydrous potassium fluoride (0.5 g), and dimethylformamide (4 cm^3) were stirred and heated under reflux for 72 h, poured into water (7 cm^3), and extracted with ether. The extracts were washed with water, dried ($MgSO_4$), and evaporated. Distillation of the residue *in vacuo* gave compound (XIIIb) (0.33 g), identified by g.l.c. and i.r. spectroscopy.

Isomerisation of a Mixture of Compounds (XIIIb) *and* (XVb).—Treatment of this mixture [1.0 g; fraction (ii) from experiment (*b*) above] as in the foregoing experiment gave compound (XIIIb) (0.6 g).

Reaction of Decafluorocyclohexene with Butane-1,4-*diol*.—Decafluorocyclohexene (22 g, 0.082 mol), sodium hydride (1.0 g, 0.042 mol), and butane-1,4-diol (40 cm^3) were stirred together for 1 h, then poured into water (60 cm^3), and the organic layer (21.3 g) was separated, dried, and distilled to give decafluorocyclohexene (8.5 g) and a mixture (11.1 g), b.p. 84—100° at 1 mmHg. The mixture (12.6 g) was separated by g.l.c. (unit 1, 120 °C, N_2 at 9 l h^{-1}) to give (i) 3-(4-*hydroxybutoxy*)*nonafluorocyclohexene* (IIId) (2.7 g), b.p. 192° (Found: C, 36.1; H, 2.8; F, 51.8. $C_{10}H_9F_9O_2$ requires C, 36.1; H, 2.7; F, 51.5%), $\nu_{max.}$ 1 740 (CF=CF) and 3 325 cm^{-1} (OH), τ 8.31 (4 H, m, $C{\cdot}CH_2{\cdot}C$), 6.50 (1 H, s, OH), 6.43 (2 H, m, $CH_2{\cdot}O$), and 5.96 (2 H, m, $O{\cdot}CH_2$) (after D_2O added, τ 8.28, 6.39, and 5.93); (ii) a mixture (2.0 g) of compounds (IIId) and (IId); and (iii) 1-(4-*hydroxybutoxy*)-*nonafluorocyclohexene* (IId) (3.5 g), b.p. 196° (Found: C, 36.1; H, 2.7. $C_{10}H_9F_9O_2$ requires C, 36.1; H, 2.7%), $\nu_{max.}$ 1 700 [CF=C(OR)] and 3 340 cm^{-1} (OH), τ 6.41 (1 H, s, OH) [after D_2O added, τ 8.26 (4 H, m, $C{\cdot}CH_2{\cdot}C$), 6.41 (2 H, m, $O{\cdot}CH_2$), and 5.66 (2 H, m, $CH_2{\cdot}O$)].

Attempted Cyclisation of Compound (IId).—Compound (IId) (1.6 g), sodium hydride (0.5 g), and dimethylformamide (10 cm^3) were stirred at 70 °C for 24 h, poured into water, and extracted with ether (3 × 10 cm^3). The ether was removed by distillation to leave a liquid (0.6 g), shown to be mainly (IId) by g.l.c. and i.r. spectroscopy.

Attempted Cyclisation of Compound (IIId).—Compound (IIId) (1.5 g), treated in a similar way, was recovered (0.5 g).

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