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NUCLEOPHILIC REACTIONS OF FLUOROOLEFINS.

I. REACTIONS OF 1-(2-TETRAHYDROFURYL)-PENTAFLUORO PROPENE WITH ALKOXIDE IONS[✽]

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SUMMARY

Unlike unsubstituted perfluoropropene [1,2] 1-(2-tetrahydrofuryl)-pentafluoropropene 1 reacts with sodium alkoxides in parent alcohol solutions to give 1-alkoxy-1-(2-tetrahydrofuryl)-tetrafluoropropenes 2 as major products and 1-alkoxy-2H-1-(2-tetrahydrofuryl)-pentafluoropropanes 3 as very minor products. The yield of adducts 3 is, to some extent, increased by the reduced basicity of the alkoxide ion. Results are discussed in terms of the supposed properties of the carbanionic intermediates involved.

N.m.r., m.s., and i.r. data for, and some chemical properties of compounds 2, viz., further reactions with sodium alkoxides and hydrolysis are described.

INTRODUCTION

Nucleophilic reactions of perfluoro- and chlorofluoro-olefins containing two to four carbon atoms in the molecule have been reported in numerous publications [1]. These olefins combine readily, preferably in the presence of basic

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catalysts, with alcohols, thiols, and phenols to give saturated ethers as major or sole products. Functional derivatives of perfluoroolefins, i.e. perfluoroacryloyl and perfluoromethacryloyl fluorides [2] and methyl perfluoroacrylate [3], react likewise with alcohols to give saturated derivatives formed by a nucleophilic attack on the terminal CF_2 groups of these compounds.

Small amounts of unsaturated ethers formed by replacement of the vinylic fluorine by alkoxy or aryloxy groups were obtained occasionally in the reactions of alcohols with low molecular weight fluorolefins [1]. The tendency of unsaturated ethers to form at the expense of adducts, observed in the reactions with perfluoroisobutene [1], increases with the rising basicity of the attacking alkoxy anion, viz., $\text{C}_2\text{H}_5\text{O} < n\text{-C}_3\text{H}_7\text{O} < \text{iso-C}_3\text{H}_7\text{O} < n\text{-C}_4\text{H}_9\text{O}$. The reactions of alcohols with branched higher perfluoroolefins, i.e. dimers [4] and trimers [5] of hexafluoropropene recently available, were reported to give unsaturated ethers exclusively, regardless of the nature of the nucleophile. It has been postulated [6] that, in nucleophilic reactions with internally branched perfluoroolefins, there is a definite tendency to form unsaturated products as a result of the rising stability of the carbanionic intermediates involved.

In order to accumulate more experimental data on the relationship between the structure of the carbanionic intermediates and the ratio of addition and elimination products, it was deemed of interest to study the nucleophilic reactions of fluorolefins in which the electron-withdrawing power of at least one vinyl substituent is lower than that of fluorine of a perfluoroalkyl group.

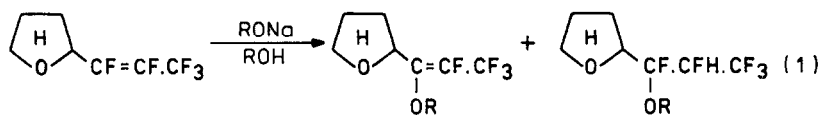
This paper sets out to describe the results of the reactions of various alcohols with 1-(2-tetrahydrofuryl)-pentafluoropropene **1**, which is relatively easily available from hexafluoropropene and tetrahydrofuran in a two-step process.

RESULTS AND DISCUSSION

1-(2-Tetrahydrofuryl)-pentafluoropropene 1 was earlier obtained in 47.2 % yield [7] by dehydrofluorination of 2H-1-(2-tetrahydrofuryl)-hexafluoropropane, which in turn can be synthesised in more than 90 % yield by either a free radical [7,8] or a potassium fluoride catalysed [9] addition of tetrahydrofuran to hexafluoropropene.

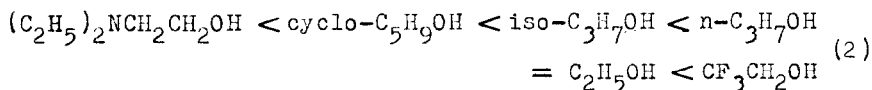
In this Laboratory the dehydrofluorination reaction has been improved by replacing the dry powdered KOH originally employed by a KOH slurry in diethyleneglycol diethyl ether or t-butanolic sodium t-butoxide as the dehydrofluorinating reagent, to give a mixture of geometric isomers of 1 in 70-80 % yield.

1-(2-Tetrahydrofuryl)-pentafluoropropene 1 reacted with sodium alkoxides in parent alcohol solutions to give mixtures of isomers Z and E of 1-alkoxy-1-(2-tetrahydrofuryl)-tetrafluoropropenes 2 and diastereoisomers of 1-alkoxy-2H-1-(2-tetrahydrofuryl)-pentafluoropropanes 3.

1232a, 2a : R = C₂H₅-2d, 3d : R = cyclo-C₅H₉-2b, 3b : R = n-C₃H₇-2e, 3e : R = CF₃CH₂-2c, 3c : R = iso-C₃H₇-2f : R = (C₂H₅)₂NCH₂CH₂-

The reactions were conducted with six alcoholic sodium alkoxides and results are summarised in Table 1. The nucleophilic attack of an alkoxide ion proceeded exclusively at the carbon atom bearing the tetrahydrofuryl substituent and 1,1-disubstituted olefins 2 were formed as the major products regardless of the nature of the alkoxide ion and reaction conditions. Adducts 3 were always formed as very minor products, although the tendency for alcohols to add across the

double bond of the olefin 1 was found to increase to some extent in the order:



i.e. as the corresponding alkoxide ions become less basic.

TABLE 1

Reactions of 1-(2-tetrahydrofuryl)-pentafluoropropene 1 with sodium alkoxides

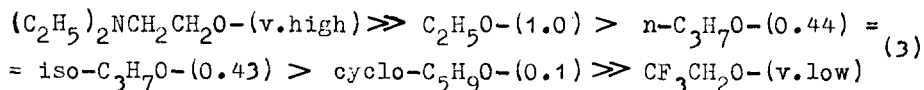
Alkoxide RO-	Reaction conditions ^a		Products(g.l.c. yields)		Z/E ratio of <u>2</u>
	temp. (°C)	time (hrs.)	<u>2</u>	<u>3</u>	
C ₂ H ₅ O-	25	8	70.0	11.6	3.4 ^b
	25	24	84.3	11.2	2.7 ^b
	60	1	82.2	10.9	
	60	3	90.0	7.6	2.0 ^b
n-C ₃ H ₇ O-	25	8	28.6	7.2	
	25	24	44.8	11.0	4.5 ^b
	60	1	59.6	13.0	
	60	3	72.6	15.0	2.5 ^b
iso-C ₃ H ₇ O-	25	8	32.0	7.2	5.8 ^c
	25	24	65.9	5.4	4.8 ^c
	60	1	64.8	5.4	3.7 ^c
	60	3	73.8	6.6	3.4 ^c
	90	6	90.3	2.5	3.0 ^c
cyclo- -C ₅ H ₉ O-	25	8	8.0	0.0	
	25	24	13.0	1.2	3.7 ^c
	60	1	16.4	3.0	3.2 ^c
	60	3	39.4	4.7	3.2 ^c
	90	6	94.4	1.1	2.2 ^c
CF ₃ CH ₂ O-	60	3	no reaction		
	90	30	49.0	16.8	
(C ₂ H ₅) ₂ NCH ₂ CH ₂ O-					
	25	1	98.0	0.0	

a) 0.01 mole 1 (Z/E=1.9), 0.02 mole Na, and 0.2 mole ROH were used in each experiment

b) estimated from integrated ¹⁹F n.m.r. spectra

c) g.l.c. estimates

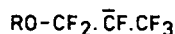
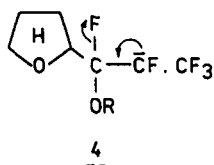
The relative reactivities of the alkoxide ions followed a different order:



However, 2-diethylaminoethoxide and 2,2,2-trifluoroethoxide ions, owing to their respectively highest and lowest basicities, were the most and the least reactive, but as is evident from the reactivity values (in parentheses), calculated as the ratios of the total yields of products obtained at 25° after 8 hours, the reactivities of other alkoxide ions investigated decrease as their molecular weights increase. Since *n*- and *iso*-propoxide ions exhibited identical reactivities, the above order can be attributed to the decreasing miscibility of the reactants in highly viscous reaction mixtures, rather than to steric or electronic factors.

Since by analogy with the corresponding reactions of perfluoroolefins [6], in the reactions of the olefin 1 with alcohols the carbanionic mechanism is the most likely to operate and the unsaturated compounds 2 are formed via elimination of the fluoride ion from intermediate carbanions 4, rather than via dehydrofluorination of adducts 3; the dehydrofluorination of 3 with parent sodium alkoxides was demonstrated in separate experiments to proceed much more slowly than does the formation of 2 from the olefin 1.

The reversal of the distribution of products in the present reactions as compared with the analogous reactions of perfluoropropene, which yield saturated adducts mainly [1,2] can be rationalised in terms of the relative abilities of the possible carbanionic intermediates 4 and 5 to eject the fluoride ion, rather than of their stabilities.



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However, by reason of the presumed difference in electronegativity between the fluorine and tetrahydrofuryl substituents, carbanions 4 may be expected to be less stable and therefore more reactive toward a proton than carbanions 5 but relatively high electron density on the carbon C-1 in carbanions 4 makes elimination of the fluoride ion to be faster than abstraction of a proton from an alcohol, to give predominantly substitution products 2. In carbanions 5 the fluorine atoms on the carbon C-1 are bonded strongly enough to make fluoride ion elimination slower than abstraction of a proton, whereby addition becomes the favoured reaction. It has been found [10] that steric factors in carbanions of the type discussed do not influence significantly the elimination-addition ratio.

The observed order (scheme 2) of the increasing tendency to form adducts 3 as the electron density on the oxygen atom of the alkoxy groups is decreased, may be interpreted both in terms of the decreasing ability of carbanions 4 to eliminate the fluoride ion and the increased acidity of the corresponding alcohols.

This reasoning is not necessarily in conflict with the known fact that alkoxyfluorocarbanions of the type $R_F CF(OR). \bar{C}(R_F)_2$, where R_F is perfluoroalkyl group, also stabilise themselves preferentially by fluoride ion elimination; this being accounted for by their low basicity, insufficient to abstract a proton from an alcohol [6].

1-Alkoxy-1-(2-tetrahydrofuryl)-tetrafluoropropenes 2 were isolated as mixtures of geometric isomers, whose elemental analyses and mass spectra (Table 2 and 3) were consistent with the predicted formulae. The mass spectra of compounds 2a-e exhibited molecular ions $[M]^+$ of low intensities and fragmentation ions of medium intensities with mass numbers: $200[M-(R-H)]^+$, $183[M-OR]^+$ and $141[C_5H_5F_4]^+$ found characteristic of this group of compounds. Compound 2f also gave a molecular ion $299[M]^+$ but except for the 2-diethylaminoethyl ion $100[C_6H_{14}N]^+$ and the ions formed by its further fragmentation no other ions were detected. The presence of a double bond was evidenced by strong i.r. absorption at $1683-1695\text{ cm}^{-1}$.

TABLE 2

Physical properties and elemental analyses of 1-alkoxy-
-1-(2-tetrahydrofuryl)-tetrafluoropropenes 2^a

Compd.	Boiling range °C (mmHg)	$\nu(\text{C}=\text{C})$ cm^{-1}	Found (%)			Calculated (%)		
			C	H	F	C	H	F
<u>2a</u>	52-54 (6)	1685	47.3	5.1	33.2	47.4	5.3	33.3
<u>2b</u>	70-72 (6)	1688	49.8	5.6	31.4	49.6	5.8	31.4
<u>2c</u>	75-76 (15)	1683	49.6	5.7	31.3	49.6	5.8	31.4
<u>2d</u>	78-80 (0.5)	1683	53.6	6.1	28.3	53.7	6.0	28.3
<u>2e</u>	60-62 (6)	1695	38.3	3.2	47.1	38.3	3.2	47.1
<u>2f</u>	64-65 (0.15)	1687	52.0	6.9	25.4	52.2	7.0	25.4

a) mixtures of isomers Z and E

TABLE 3

Mass spectra of 1-alkoxy-1-(2-tetrahydrofuryl)-tetrafluoro-
propenes 2 and 1-alkoxy-2H-1-(2-tetrahydrofuryl)-pentafluoro-
propanes 3

Compound	m/e (relative intensity) ^a
<u>2a</u>	288(4.6)[M] ⁺ , 200(3.2), 183(45.1), 141(33.9), 139(8.9), 131(13.2), 115(17.9), 71(100.0), 69(16.6), 43(64.5), 42(90.2), 41(52.0), 39(24.1), 29(81.1), 27(63.7)
<u>2b</u>	242(1.8)[M] ⁺ , 200(23.2), 183(17.8), 160(5.8), 141(10.8), 139(17.2), 131(13.4), 71(29.8), 69(6.6), 43(100.0), 42(62.8), 41(56.8), 39(17.7), 29(6.6), 27(37.9)
<u>2c</u>	242(1.0)[M] ⁺ , 200(29.8), 183(31.0), 160(7.1), 141(20.1), 139(25.1), 131(19.0), 115(7.1), 71(55.9), 69(11.0), 43(100.0), 42(98.9), 41(59.6), 39(24.3), 29(32.0), 27(49.0)
<u>2d</u>	268(0.9)[M] ⁺ , 200(18.9), 183(14.0), 160(5.9), 141(5.0), 139(13.2), 131(9.7), 71(15.4), 69(60.0), 68(32.1), 67(27.0), 43(18.0), 42(69.0), 41(100.0), 39(23.8), 29(6.7), 27(16.4)

(continued on following page)

TABLE 3 (continued)

<u>2e</u>	282(6.8)[M] ⁺ , 221(24.2), 213(8.1), 183(100.0), 141(60.8), 83(30.9), 71(68.5), 69(12.4), 43(33.2), 42(73.4), 41(35.0), 39(16.0), 29(14.9), 27(16.6)
<u>2f</u>	299(1.8)[M] ⁺ , 100(7.4), 86(100.0), 58(8.0), 56(7.7), 44(6.3), 42(9.2), 31(5.8), 29(6.9)
<u>3a</u>	229(0.3)[M-F] ⁺ , 228(0.3), 203(0.5), 201(0.5), 147(0.7), 101(2.1), 71(100.0), 69(3.9), 43(54.4), 42(10.6), 41(21.0), 39(6.5), 29(26.3), 27(20.7)
<u>3b</u>	243(2.0)[M-F] ⁺ , 233(1.3), 203(4.6), 201(6.0), 161(6.5), 133(14.4), 119(6.9), 101(6.4), 91(6.9), 72(29.3), 71(97.5), 69(14.5), 51(16.7), 43(96.4), 42(27.9), 41(100.0), 39(38.0), 29(19.8), 28(9.3), 27(81.2)
<u>3c</u>	203(2.9)[M-C ₃ H ₇ O] ⁺ , 201(0.7), 161(2.2), 133(3.3), 101(1.5), 71(100.0), 69(2.9), 43(81.9), 42(8.5), 41(31.5), 39(9.2), 29(5.8), 28(4.8), 27(18.4)
<u>3d</u>	242(2.6)[M-C ₂ H ₃ F] ⁺ , 201(9.0), 189(4.3), 136(15.6), 121(8.6), 111(5.7), 101(20.3), 107(12.2), 95(31.6), 94(26.2), 93(23.4), 82(18.1), 81(17.4), 80(21.7), 79(20.2), 71(55.0), 69(45.3), 68(45.7), 67(65.7), 57(31.9), 55(31.4), 54(12.4), 53(16.9), 44(12.0), 43(50.3), 42(9.5), 41(100.0), 40(9.0), 39(34.8), 29(28.3), 28(12.8), 27(40.5)
<u>3e</u>	283(0.3)[M-F] ⁺ , 213(4.4), 203(0.4), 201(4.3), 133(3.0), 131(5.1), 101(2.5), 83(27.1), 71(100.0), 69(7.1), 51(5.7), 43(88.3), 42(10.9), 41(41.7), 39(10.8), 29(11.1), 27(17.6)

a) Spectra of the most abundant isomers are given. All ions with relative intensities exceeding 5 % and the most characteristic ions of lower intensities are quoted.

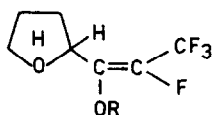
As expected from the presence of three asymmetric centres in their molecules, 1-alkoxy-2H-1-(2-tetrahydrofuryl)-pentafluoropropanes **2** appeared in four diastereoisomeric forms distinguished by gas-liquid chromatography. These compounds were formed in quantities too small to be isolated and were identified by g.l.c.-mass spectra only. However, no molecular ions were observed and these compounds were identified by following the ions of low intensities: $[M-F]^+$, $203[M-OR]^+$, $201[M-F-(R-H)]^+$, $[M-C_2F_4H]^+$ and $101[C_2F_4H]^+$, for each isomer.

N.m.r. studies on mixtures of the Z and E isomers of compounds **2** allowed them to be distinguished. The ^{19}F n.m.r. spectra of these mixtures (Table 4) consisted of two signals for CF_3 groups (doublets) and two signals for vinylic fluorines. The upper field signals of vinylic fluorines exhibited long-range coupling to C-2 ring proton (quartets of doublets, $^3J(FF) = 9.2 - 10.0$ Hz, $^4J(HF) = 4.0 - 4.6$ Hz), not observed in the lower field signals (quartets); therefore, the former signals were assigned to isomers E, in which this fluorine and tetrahydrofuran ring are *cis* to each other, and the latter signals to isomers Z. The vinylic fluorine quartets of isomers Z showed a fine multiplet structure because of the through space couplings to atoms of substituents RO-; compound **2e** exhibited further splitting of the CF_3 triplets of the CF_3CH_2O- group by the vinylic fluorine (triplet of doublets, $^3J(HF) = 8.4$ Hz, $^6J(FF) = 2.0$ Hz) in the isomer Z, or by the CF_3 group (triplet of quartets, $^3J(HF) = 8.7$ Hz, $^7H(FF) = 2.0$ Hz) in the isomer E. It was established from the relative intensities that the ^{19}F n.m.r. signals due to vinylic fluorines and CF_3 groups of isomers Z appeared characteristically at a slightly lower field than those for the E form.

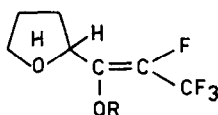
The ratios of the Z and E isomers of compounds **2** were determined in the crude samples from the integrated ^{19}F n.m.r. spectra (relative intensities of CF_3 group signals) or, if possible, by g.l.c.; the isomer Z had shorter retention in the gas chromatogram of each sample. The Z/E ratio varied with the nature of the substituent RO- and the reaction conditions but,

TABLE 4

^{19}F n.m.r. data of 1-alkoxy-1-(2-tetrahydrofuryl)-tetrafluoropropenes 2



Z



E

Compound		Chemical shift (ppm) ^a		Coupling constant (Hz)	
		$\delta(\text{CF}_3)$	$\delta(\text{F})$	$^3J_{\text{F-CF}_3}$	$^4J_{\text{F-H}}$
<u>2a</u>	Z	63.4 (d)	154.4 (qm)	9.7	
	E	67.5 (d)	160.5 (qd)	9.4	4.5
<u>2b</u>	Z	63.4 (d)	155.0 (qm)	9.2	
	E	67.5 (d)	160.4 (qd)	9.2	4.2
<u>2c</u>	Z	62.6 (d)	153.6 (qm)	9.5	
	E	66.1 (d)	160.1 (qd)	10.0	4.0
<u>2d</u>	Z	62.8 (d)	154.8 (qm)	9.5	
	E	66.5 (d)	160.1 (qd)	9.5	4.0
<u>2e</u>	Z	64.5 (d) ^b	149.9 (qm)	9.2	
	E	67.7 (dq) ^c	156.3 (qd)	9.2	4.0
<u>2f</u>	Z	63.3 (d)	154.7 (qm)	9.8	
	E	67.2 (d)	161.1 (qd)	9.8	4.6

d - doublet, t - triplet, q - quartet, m - multiplet

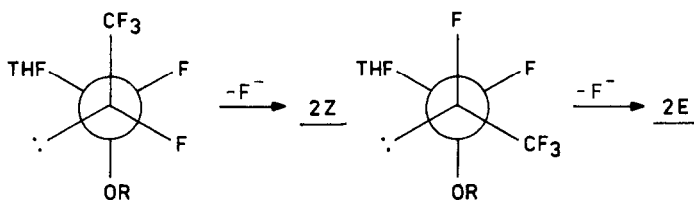
a) positive upfield from CCl_3F

b) $\delta(\text{CF}_3\text{CH}_2) = 75.9$ (td)

c) $\delta(\text{CF}_3\text{CH}_2) = 75.4$ (tq)

in general, differed from that in the starting olefin 1 to favour of the isomer Z, even under thermodynamic conditions (Table 1).

The predominant formation of isomers Z, particularly under kinetic conditions (25°) and with the resulting compounds 2 containing bulky substituents RO-, can be interpreted in terms of conformational stability of the carbanionic intermediates involved:

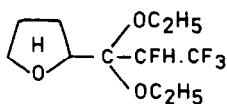
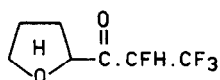


THF = tetrahydrofuryl

Consideration of steric and electronic repulsions between the alkoxy and CF₃ groups suggests that the conformation yielding the isomer Z by trans-elimination of the fluoride ion should be energetically preferable to that leading to the isomer E.

However, the stereochemistry of the substitution reaction is not clear and in the stages far from the completion the Z/E ratio of products 2 may well be strongly affected by the excess of the Z form (Z/E = 1.9) in the starting olefin 1 especially that the reaction of this isomer with alkoxide ions was found to be faster than that of the E form: these facts seem to contribute significantly to the predominant formation of products 2Z under the conditions where a considerable amount of the olefin 1 remained unreacted.

Compounds 2 were found to be susceptible to further attack by alkoxide ions, although drastic reaction conditions had to be applied, e.g. 2a on prolonged treatment with saturated hot ethanolic sodium ethoxide added the alcohol to give a mixture of diastereoisomers of 1,1-diethoxy-2H-1-(2-tetrahydrofuryl)-tetrafluoropropane 6 in 35 % yield.

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Compounds 2 are sensitive to acids and, when treated with concentrated hydrochloric acid at 20°, hydrolysed to give diastereoisomers of 2-(2,3,3,3-tetrafluoropropionyl)-tetrahydrofuran 7 quantitatively.

The ¹⁹F n.m.r. spectra of compounds 6 and 7 (see Experimental) exhibited typical geminal coupling constants ²J(HF) = 48.5 and 41.0 Hz, respectively, identical for either diastereoisomer. ¹⁹F and ¹H n.m.r. spectra of the longer g.l.c. retention diastereoisomer of compound 7, similarly to compounds 2E, exhibited long range coupling of the CHF fluorine to the C-2 ring proton (⁴J(HF) = 2.5 Hz); this coupling was observed neither with the second diastereoisomer of 7 nor with any diastereoisomer of compound 6.

EXPERIMENTAL

N.m.r. spectra were recorded with a JEOL JNM-4H-100 spectrometer; chemical shifts are in p.p.m. from internal CCl₃F for ¹⁹F spectra (positive upfield) and from internal TMS for ¹H spectra (positive downfield). Mass spectra were obtained with an Analytical GCMS System LKB-2091 and i.r. spectra were recorded with a Beckmann IR 4240 spectrometer. G.l.c. analyses were performed with a Chromatron GCHF.18.3.4 instrument (G.D.R.) equipped with a polyethylene glycol adipate (PEGA, 3%) - on-Chromosorb G column, 3.5 m long.

2H-1-(2-Tetrahydrofuryl)-hexafluoropropane was prepared according to the procedure described previously [8].

Dehydrofluorination of 2H-1-(2-tetrahydrofuryl)-hexafluoropropane

a) with KOH

2H-1-(2-tetrahydrofuryl)-hexafluoropropane (22.0 g, 0.1 mole), powdered KOH (15 g, 0.27 mole), and dry diglyme (50 ml) were stirred together at 110-120° for 8 hours and the reaction mixture was subjected to distillation. The distillate (boiling range 80-140°) containing the resulting olefin **1**, diglyme, and a small amount of water evolved in the reaction was diluted with water and the bottom organic layer was separated and dried over MgSO₄. Distillation gave 1-(2-tetrahydrofuryl)-pentafluoropropene **1**, b.p. = 128-130°, (15 g, yield 75.0 %) of 96.5 % purity (Z/E = 1.9), contaminated with 3.5 % of the unaltered reactant (g.l.c. estimate).

A similar run at 60-70° for 20 hours gave **1** in 72.7 % yield.

b) with sodium t-butoxide

2H-1-(2-tetrahydrofuryl)-hexafluoropropane (18.0 g, 0.08 mole) was added to a solution of sodium metal (3.6 g, 0.156 mole) in t-butyl alcohol (90 ml). The reaction mixture was stirred at 25° for 7 hours then diluted with water and neutralised by hydrochloric acid. The organic layer was separated, dried over MgSO₄, and distilled to give 13.0 g of a product containing 88.0 % (yield 70.8 %) of the olefin **1** (Z/E = 1.15) and 12.0 % of the unaltered reactant.

General procedure for the reaction of 1-(2-tetrahydrofuryl)-pentafluoropropene **1** with sodium alkoxides

Sodium alkoxide solutions prepared from sodium metal (0.5 g, 0.02 mole) and an appropriate alcohol (0.20 mole) were warmed up to the required reaction temperature and then 1-(2-tetrahydrofuryl)-pentafluoropropene **1** (2.0 g, 0.01 mole) was added as one portion with stirring. In the course of the reaction, small samples (0.2-0.5 ml) of the mixture were taken, diluted with water, acidified with hydrochloric acid and the separating organic layer was analysed by g.l.c. . Finally, the reaction mixture was diluted with water, adjusted with hydrochloric acid to pH = 7.5, and the organic material

was extracted with ether. The extract was dried with MgSO_4 , the solvent removed and the residue subjected to g.l.c. and m.s. analyses. Samples of 1-alkoxy-1-(2-tetrahydrofuryl)-tetrafluoropropenes 2 (mixtures of Z and E forms) for elemental analysis, n.m.r. and i.r. investigations were prepared by distillation; analytical and spectral data are given in Tables 2, 3, and 4.

Reaction of 1-ethoxy-1-(2-tetrahydrofuryl)-tetrafluoropropene 2a with sodium ethoxide

1-Ethoxy-1-(2-tetrahydrofuryl)-tetrafluoropropene 2a (2.4 g, 0.0205 mole) and a saturated sodium ethoxide solution prepared from 0.6 g (0.026 mole) of sodium metal and 5 ml of ethanol were stirred together and heated at 80° for 15 hours and then worked up as described above. A mixture of the reaction products was shown by g.l.c. to contain 49 % of the unreacted 2a, 35 % of diastereoisomers (2 : 1) of 1,1-diethoxy-2H-1-(tetrahydrofuryl)-tetrafluoropropane 6, and 16 % of higher molecular weight substances. Distillation gave a fraction (b.p. $74-86^\circ$, 4mmHg) containing 72 % of compound 6.

^{19}F and ^1H n.m.r. for diastereoisomer 6A: $\delta(\text{CF}_3) = 72.1$ ppm(dd), $\delta(\text{CHF}) = 204.8$ ppm(dq), $\delta(\text{CHF}) = 5.22$ ppm(dq), $^2\text{J}(\text{HF}) = 48.5$ Hz, $^3\text{J}(\text{FF}) = 10.2$ Hz, $^3\text{J}(\text{HF}) = 7.4$ Hz; for diastereoisomer 6B:

$\delta(\text{CF}_3) = 72.4$ ppm(dd), $\delta(\text{CHF}) = 206.2$ ppm(dq), $\delta(\text{CHF}) = 5.22$ ppm(dq), $^2\text{J}(\text{HF}) = 48.5$ Hz, $^3\text{J}(\text{FF}) = 9.4$ Hz, $^3\text{J}(\text{HF}) = 7.4$ Hz.

M.s. : 232 (9%) [$\text{C}_8\text{H}_{12}\text{F}_4\text{O}_3$] $^+$, 203 (23%) [$\text{C}_6\text{H}_7\text{F}_4\text{O}_3$] $^+$, 187 (20%) [$\text{C}_6\text{H}_7\text{F}_4\text{O}_2$] $^+$, 186 (12%) [$\text{C}_6\text{H}_6\text{F}_4\text{O}_2$] $^+$, 157 (27%) [$\text{C}_4\text{H}_4\text{F}_4\text{O}_2$] $^+$, 142 (22%) [$\text{C}_4\text{H}_2\text{F}_4\text{O}$] $^+$, 114 (31%) [$\text{C}_3\text{H}_2\text{F}_4$] $^+$, 71 (100%) [$\text{C}_4\text{H}_7\text{O}$] $^+$, 29 (90%) [C_2H_5] $^+$

Hydrolysis of 1-alkoxy-1-(2-tetrahydrofuryl)-tetrafluoropropenes 2

Compound 2 (0.02 mole) and concentrated hydrochloric acid (10 ml) were stirred together at 20° for 18 hours, then neutralised with Na_2CO_3 , and extracted with ether. The ether was distilled off and the residue was found by g.l.c. to contain two new substances but no unreacted 2. Distillation gave a mixture of diastereoisomers (10 : 12) of 2-(2,3,3,3-tetrafluoropropionyl)-tetrahydrofuran 7 of 99 % purity.

Boiling range 52-55° (6 mmHg). Found: C - 42.3 %, H - 3.7 %, F - 37.9 %. Calculated for $C_7H_8F_4O_2$: C - 42.0 %, H - 4.0 %, F - 38.0 %. M.s. : 180 (1.3 %) $[M-HF]^+$, 172 (1.7 %) $[C_5H_4F_4O_2]^+$, 104 (9 %) $[C_2H_4F]^+$, 71 (100 %) $[C_4H_7O]^+$. I.r. : $\nu(C=O) = 1745 \text{ cm}^{-1}$ ^{19}F and 1H n.m.r. for diastereoisomer 7A: $\delta(CF_3) = 75.0 \text{ ppm}(\text{dd})$, $\delta(\underline{CHF}) = 208.6 \text{ ppm}(\text{dq})$, $\delta(\underline{CHF}) = 5.33 \text{ ppm}(\text{dq})$, $^2J(\text{HF}) = 41.0 \text{ Hz}$, $^3J(\text{FF}) = 11.0 \text{ Hz}$, $^3J(\text{HF}) = 6.7 \text{ Hz}$; for diastereoisomer 7B: $\delta(CF_3) = 75.2 \text{ ppm}(\text{dd})$, $\delta(\underline{CHF}) = 207.3 \text{ ppm}(\text{dq})$, $\delta(\underline{CHF}) = 5.45 \text{ ppm}(\text{dq})$, $^2J(\text{HF}) = 41.0 \text{ Hz}$, $^3J(\text{FF}) = 11.0 \text{ Hz}$, $^3J(\text{HF}) = 6.7 \text{ Hz}$, $^4J(\text{HF}) = 2.5 \text{ Hz}$

2,4-Dinitrohydrazone, m.p. = 135-136°

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