Journal of Fluorine Chemistry, 18 (1981) 223–241
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Received: February 2, 1981

PREPARATION OF SOME HIGHLY HALOGENATED DERIVATIVES OF FURAN

W.DMOWSKI and H.VOELLNAGEL-NEUGEBAUER

Institute of Organic Chemistry, Polish Academy of Sciences,
00-961 Warsaw (Poland)

SUMMARY

Direct chlorination of 2-(2H-hexafluoropropyl)-tetrahydrofuran 1 gave high yield of 2-(2-chlorohexafluoropropyl)-pentachloro-2,5-dihydrofuran 2. Bromination of 1 gave very complex mixture of products, from which three compounds, viz. 2-bromo-5-(2H-hexafluoropropyl)-furan 3, 3-bromo-5-(2H-hexafluoropropyl)-furan 4, and 2,4-dibromo-5-(2H-hexafluoropropyl)-furan 5 were isolated. Exchange fluorination of 2 with dry KF at 240 - 300° led to a stepwise substitution of fluorines for chlorines to give mixtures of chloro-fluoro-2-(2-chlorohexafluoropropyl)-dihydrofurans 7,8,9 and 10, together with small amounts of 2-(2-chlorohexafluoropropyl)-3,4,5-trichlorofuran 6.

Exchange fluorination of 3,4-dihalo-2,2,5,5-tetrafluoro-2,5-dihydrofurans 11a and 11b led to a substitution of fluorine for one vinylic halogen to give 3-halo-2,2,4,5,5-pentafluoro-2,5-dihydrofurans 12a and 12b in good yields.

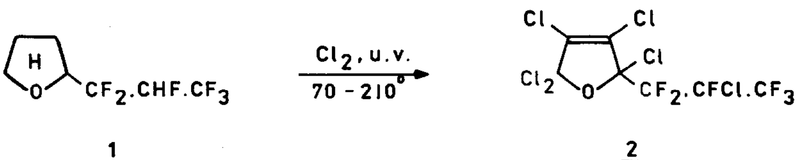
Compounds 2 - 12 were characterised by n.m.r., m.s., and i.r. spectroscopy and elemental analysis.

INTRODUCTION

The exchange fluorination of perchloroaromatic compounds with anhydrous potassium fluoride is well known as a general and highly efficient method of preparation of aromatic fluorocarbons and their N-heterocyclic analogues [1]. The use of a halogen exchange method to the preparation of highly fluorinated O-heterocyclic compounds has received much less attention and, to the best of the author's knowledge, the reaction of hexachloro-2,5-dihydrofuran with KF in N-methylpyrrolidone to give hexafluoro-2-5-dihydrofuran (49% yield), and with SbF_3 or mixed antimony halides to give partially fluorinated products are the only reported examples [2]. Chlorinated precursors of cyclic perfluoroethers are not easily available because exhaustive chlorination of e.g. tetrahydrofuran or dioxane leads to the cleavage to form highly chlorinated alkanecarboxylic acids [3]. Chlorination of furan at -40° afforded a mixture of mono-,di-, and trichlorofurans, but only very small quantities of tetrachlorofuran and hexachloro-2,5-dihydrofuran were isolated [4] . Hexachloro-2,5-dihydrofuran may be prepared in considerable quantities only from hexachlorobuta-1,3-diene <u>via</u> ethoxylation, chlorination, and $FeCl_3$-catalysed cyclization [5].

RESULTS AND DISCUSSION

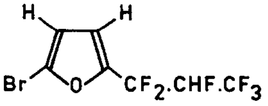
We have found, that 2-(2H-hexafluoropropyl)-tetrahydrofuran 1, which is readily available from either a free radical [6,7] or a potassium fluoride catalysed [8] addition of tetrahydrofuran to hexafluoropropene, may be directly chlorinated under extreme conditions without ring opening. Thus, prolonged chlorination of 1 at 70 - 210° under u.v. irradiation gave 2-(2-chlorohexafluoropropyl)-pentachloro-2,5-dihydrofuran 2, quantitatively. Although,the position of the double bond in the chlorinated product could not be

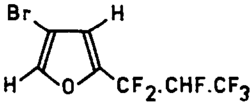


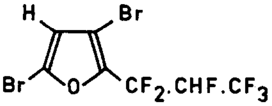
1 2

assigned directly from spectral data, the existence of two diastereoisomeric forms of this product (1:1), which are distinguished by ^{19}F n.m.r. spectroscopy, indicates saturation at the ring carbon C-2 and therefore suggests the structure 2.

Bromination of 1 at 60 - 150° gave a very complicated mixture, which by g.l.c. - m.s. analysis was found to consist of five groups of compounds of general formulae: $C_7H_7BrF_6O$, $C_7H_6Br_2F_6O$, $C_7H_5BrF_6O$, $C_7H_3BrF_6O$, and $C_7H_2Br_2F_6O$. Three relatively volatile compounds, which appeared on the g.l.chromatogram as separate peaks, were isolated and identified by spectral methods and elemental analysis. They were (in order of increasing g.l.c. retentions): 2-bromo-5-(2H-hexafluoropropyl)-furan 3, 3-bromo-5-(2H-hexafluoropropyl)-furan 4, and 2,4-dibromo-5-(2H-hexafluoropropyl)-furan 5.


3


4

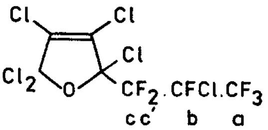
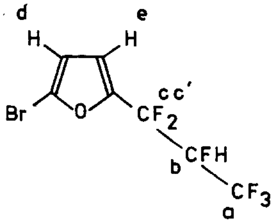

5

^{19}F and ^{1}H n.m.r. spectra of compounds 3,4,and 5 (Table 1) resembled those of 1. ^{1}H n.m.r. spectra exhibited characteristic signals at 5.0 - 5.2 ppm as doublets with geminal H - F coupling (^{2}J = 44 - 46 Hz), indicating that 2H-hexafluoropropyl substituent remained unaffected in the course of the bromination reaction. The positions of protons in the furan ring of these compounds were established from ^{1}H n.m.r. spectra by comparison with data published for furan [9] ; moreover, one of the ring protons of 3 and 4 exhibited long-range coupling ($J<1$) to fluorines of the fluoropropyl substituent which suggests position 4 for these protons. Complexity of the mixture of products obtained from bromination of 1 makes this reaction of no preparative value.

Attempted fluorination of 2-(2-chlorohexafluoropropyl)-pentachloro-2,5-dihydrofuran 2 with potassium fluoride in high boiling aprotic solvents failed; dechlorination of the ring took place and 2-(2-chlorohexafluoropropyl)-3,4,5-

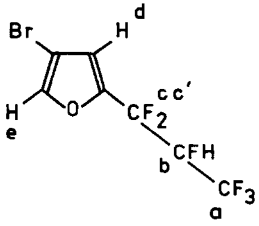
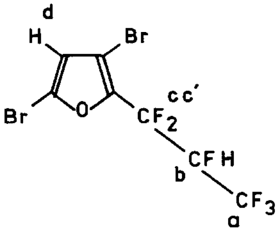
TABLE 1

^{19}F and ^{1}H n.m.r. spectra of compounds 2 - 12

Compound	Chemical shift^{a} (p.p.m.)	Coupling constant^{b} (Hz)
2, (two isomers)	F_c $F_{c'}$ two AB quartets centered at 107	$F_cF_{c'}$ = 273
	F_b 133.7 and 134.7 qn	F_bF_a = F_bF_c = 6.3
	F_a 77.5 m	
3	H_d 6.4 d	H_cH_d = 3.5
	H_c 6.7 dm	
	F_c 105.1 AB	$F_cF_{c'}$ = 290
	$F_{c'}$ 113.4	
	F_b 210.6 dm	F_bH_b = 44.2
	H_b 5.0 ddqn	H_bF_c = 12.2 H_bF_a = $H_bF_{c'}$ = 6.1
	F_a 74.6 qd	F_aF_b = F_aF_c = $F_aF_{c'}$ = 10.4

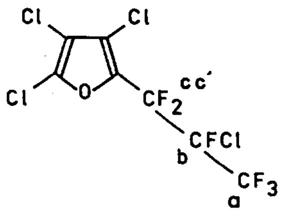
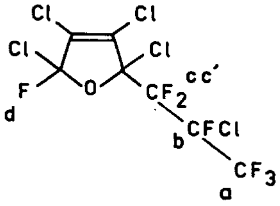
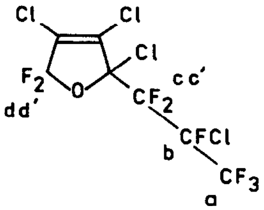
(continued on facing page)

TABLE 1 (continued)

4 	H_e	7.5	d	H_dH_e = 1.5
	H_d	6.6	m	
	F_c	105.7	AB	$F_cF_{c'}$ = 290
	$F_{c'}$	112.2		
	F_b	211.1	dm	F_bH_b = 44.0
	H_b	5.1	dddq	H_bF_c=12.0,$H_bF_{c'}$=7.3 H_bF_a = 6.0
	F_a	74.6	dtd	$F_aF_{c'}$= 10.3 F_aF_b = F_aF_c= 8.8
5 	H_d	6.5	s	
	F_c	104.9	AB	$F_cF_{c'}$= 300
	$F_{c'}$	113.3		
	F_b	210.8	dm	F_bH_b = 46.2
	H_b	5.1	ddqn	H_bF_c = 12.0 H_bF_a=$H_bF_{c'}$= 6.0
	F_a	74.6	qd	F_aF_b= F_aF_c =$F_aF_{c'}$= = 10.4

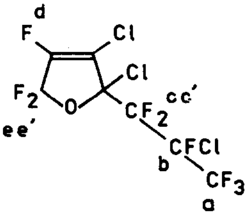
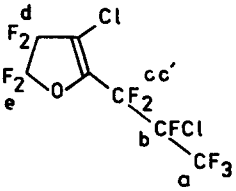
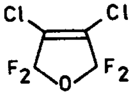
(continued overleaf)

TABLE 1 (continued)

6 	F_c $F_{c'}$	106.2 108.1 } AB	$F_cF_{c'}$ = 285
	F_b	137.5 ddq	F_aF_c=F_bF_c = 11.0
	F_a	77.6 dd	$F_aF_{c'}$=$F_bF_{c'}$=9.3
			F_aF_b = 6.7
7 (four isomers) 	F_d	47.3 d(J=4), 47.5 s, 53.0 m, and 53.4 m	
	F_c $F_{c'}$	four complex AB quartets centered at 107.7	$F_cF_{c'}$=275(approx.)
	F_b	133.0, 133.5, 133.5, and 134.0 (quintets)	F_bF_a= F_bF_c= 6.3
	F_a	77.1 m	
8 (two isomers) 	F_d $F_{d'}$	67.3 d 72.0 dd } and 67.3 d 72.1 d } AB	$F_dF_{d'}$= 150 F_dF_c= 0 and 5
	F_c $F_{c'}$	two complex AB quartets centered at 108	$F_cF_{c'}$ = 275 (approx.)
	F_b	134.7 two quintets	F_bF_a = F_bF_c= = 6.3
	F_a	77.6 m	

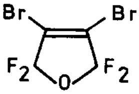
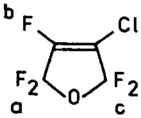
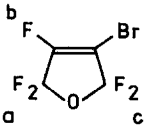
(continued on facing page)

TABLE 1 (continued)

9 (two isomers) 	F_e 68.1 $F_{e'}$ 76.1 two AB systems	$F_eF_{e'}$ = 148 F_eF_d = 8.3 $F_{e'd}$ 2 Hz
	F_d 135.9 m	
	F_c $F_{c'}$ complex systems centered at 115	
	F_b 136.4 two quintets	F_bF_a=F_bF_c= 6.5
	F_a 77.5 m	
10 	F_e 94.8 s	
	F_d 118.4 s	
	F_c $F_{c'}$ AB quartet centered at 114.5	$F_cF_{c'}$= ca. 285
	F_b 140.7	
	F_a 77.4 td	F_aF_c=$F_aF_{c'}$=10.0 F_aF_b = 7.6
11a 	F 76.1 s	

(continued overleaf)

TABLE 1 (continued)

11b 	F 73.8 s	
12a 	F_a 79.0 dt F_b 137.5 tt F_c 75.7 dt	F_aF_b = 13.5, F_aF_c = 4.2 F_bF_c = 6.7
12b 	F_a 79.1 dt F_b 133.5 tt F_c 73.8 dt	F_aF_b = 13.6, F_aF_c = 4.2 F_bF_c = 6.8

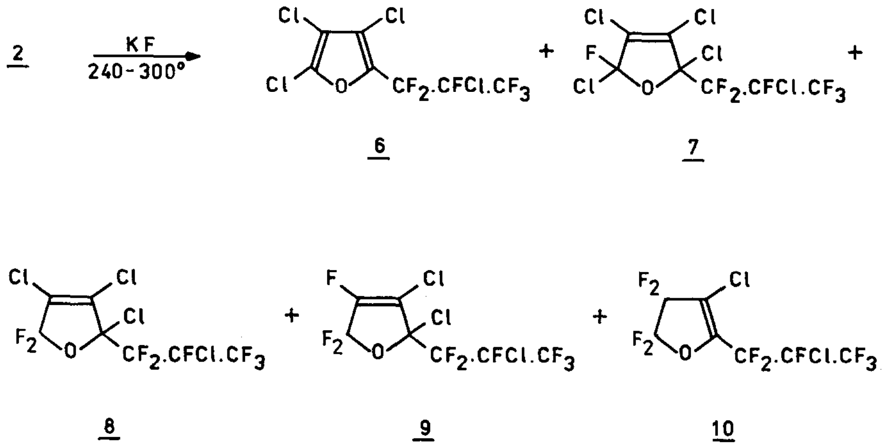
d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet;

[a] positive upfield from CCl_3F for ^{19}F and downfield from TMS for ^1H;

[b] only obvious coupling constants are quoted.

-trichlorofuran 6 was formed as the main product. It was proved by heating of 2 in a solvent at 150 -200°, that dechlorination proceeds also in the absence of potassium fluoride.

However, it has been found that prolonged heating of 2 with an excess of dry powdered potassium fluoride in an autoclave at 240 - 300° leads to a stepwise substitution of chlorine atoms in the furan ring by fluorines to give mixtures of chloro-fluoro-2-(2-chlorohexafluoropropyl)-dihydrofurans 7,8,9 and 10, together with only small amounts of the dechlorinated product 6 .



The results are summarised in Table 2. In the temperature range 240 - 280°, 2-(2-chlorohexafluoropropyl)-5-fluoro-2,3,4,5-tetrachloro-2,5-dihydrofuran 7 was obtained as the main component of the reaction mixture. Increased temperature (300°) and prolonged reaction time gave rise to higher fluorinated products 8,9, and 10. Perfluorinated products were not obtained because further increase of temperature or prolongation of the reaction time led to a substantial carbonisation of the organic material.

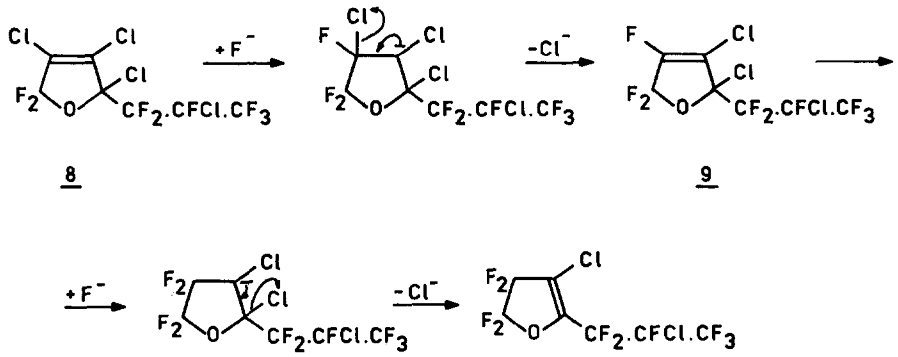
TABLE 2

Fluorination of 2-(2-chlorohexafluoropropyl)-pentachloro-2,5-dihydrofuran 2 with dry potassium fluoride

Reaction conditions temp. (°C)	Reaction conditions time (hrs)	Yield of products (%)[a]	Major components of the reaction mixture (g.l.c.%) 2	6	7	8	9	10
240	30	74.1	78.0	1.6	14.5			
260	16	70.6	77.0	2.2	16.0			
280	16	75.3	29.0	3.8	51.2	8.0		
300	16	70.5	1.2	7.2	38.5	38.1		
300	20	68.2		2.5	13.4	75.3	3.8	
300	25	55.3				1.8	50.7	43.3

[a] weight % of the substrate 2

Structure of compounds 7 - 10 suggests that in the exchange fluorination reactions, two mechanisms are involved. Substitution of chlorines bonded to sp^3 ring carbon of 2 to form compounds 7 and 8 proceeds most probably via a simple S_{N2} mechanism, while further fluorination of 8 to give 9 and 10 involves a sequence of addition-elimination reactions as follows :



8

9

10

Compounds 6 - 10 were isolated by preparative g.l.c. and identified by elemental analysis and spectral methods. The ^{19}F n.m.r. spectra (Table 1) of compounds 8 and 9 exhibited double signals for the ring CF_2 group and for side chain fluorines, indicating therefore the appearance of two diastereoisomeric forms of these compounds. The ring CF_2 group of 8 and 9 form an AB spin system with J(AB) = 150 and 148 Hz,respectively i.e. within the range which in series of alkyl substituted perfluorooxanes and perfluorooxolanes, has been found characteristic of geminal fluorines at an α carbon to oxygen [10] . The occurrence of four signals for each group of fluorines in the n.m.r. spectrum of 7, indicates that this compound appears as a mixture of four diastereoisomers. The position of the vinylic fluorine in compound 9 has been evidenced by coupling to the neighbouring AB fluorines (^3J = 8.3 and ca. 2 Hz). The location of the vinylic fluorine is also confirmed by consideration of a possible substitution mechanism, as discussed above.

Compound 10, as seen from its n.m.r. spectrum, did not exhibit diastereoisomers. It means a lack of a second asymetric centre in this molecule, besides CFCl group in the side chain, and therefore, position 2,3 must be assigned to the double bond in compound 10. No coupling between vicinal fluorines of the ring CF_2 groups of 10 was observed; this is a common feature for saturated perfluorinated compounds.

The mass spectra (Table 3) of the majority of compounds 2 - 10 exhibited molecular ions of high intensities. The most characteristic ions for compounds 3,4,5,6,and 10, in which the hexafluoropropyl substituent was attached to the ring sp^2 carbon, were those formed by elimination of CF_3CFH or CF_3CFCl fragments. For compounds 2,7,8, elimination of halogens, and for compound 9 elimation of $CF_3CFClCF_2$ group seemed to be characteristic behaviour.

We also carried out the exchange fluorination of 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran 11a [11, 12] and 3,4-dibromo- 2,2,5,5-tetrafluoro-2,5-dihydrofuran 11b , conveniently prepared from dichloro- and dibromo-maleic anhydrides by reaction with sulphur tetrafluoride. Thus, treatment of 11a and 11b with potassium fluoride in dimethyl-

TABLE 3.

Boiling points, infrared and mass spectra and analyses of compounds 2 - 12.

Compd. nr.	Formula	B.p. (°C)	I.R. $V_{C=C}$(cm^{-1})	Mass spectra m/e (rel.intensity)ion^a	Analysis: found(calculated) C (%)	X^b (%)	F (%)
2	$C_7Cl_6F_6O$	237-8	1640	389(62)[M-Cl]$^+$, 219(61) [$C_5Cl_3^{35}F_2O$]$^+$	20.0(19.7)	50.0(49.9)	26.7(26.7)
3	$C_7H_3BrF_6O$			296(11)M$^{+\cdot}$, 195(53)[$C_5H_2Br^{79}F_2O$]$^+$,117(100)[$C_3H_2Br^{79}$]$^+$	28.1(28.3)	27.2(27.0)	37.6(38.4)
4	$C_7H_3BrF_6O$	163		296(19)M$^{+\cdot}$, 195(100) [$C_5H_2Br^{79}F_2O$]$^+$	28.5(28.3)	27.1(27.0)	38.4(38.4)
5	$C_7H_2Br_2F_6O$			374(13)M$^{+\cdot}$, 273(51) [$C_5HBr_2^{79}F_2O$]$^+$	22.2(22.4)	42.7(42.5)	30.3(30.3)
6	$C_7Cl_4F_6O$	195-6	1550 1610	354(30)M$^{+\cdot}$, 219(100) [$C_5Cl_3^{35}F_2O$]$^+$	23.5(23.6)	39.7(39.8)	31.9(32.0)

7	$C_7Cl_5F_7O$		1635	408(0.9)$M^{+\cdot}$, 373(79) $[C_7Cl_4^{35}F_7O]^+$	20.3(20.5)	43.6(43.2)	32.6(32.4)
8	$C_7Cl_4F_8O$	183-4	1655	392(0.3)$M^{+\cdot}$, 354(34) $[C_7Cl_4^{35}F_6O]^+$	21.1(21.3)	36.1(36.0)	38.8(38.8)
9	$C_7Cl_3F_9O$		1650	376(1.4)$M^{+\cdot}$, 191(100) $[C_4Cl_2^{35}F_3O]^+$	22.1(22.2)	28.3(28.2)	45.1(43.3)
10	$C_7Cl_2F_{10}O$			360 $M^{+\cdot}$, 225 $[C_5Cl^{35}F_6O]^+$	23.0(23.3)	19.5(19.6)	52.9(52.6)
11a	$C_4Cl_2F_4O$	73.5	1662	210(34)$M^{+\cdot}$, 163(82) $[C_3Cl_2^{35}F_3]^+$	22.1(22.8)	33.5(33.7)	35.9(36.0)

(continued on following page)

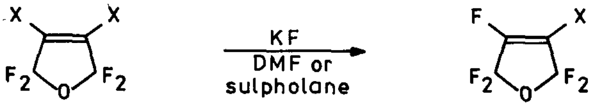
TABLE 3 (continued)

11b	$C_4Br_2F_4O$	110.5	1650	$298(33)M^{+\cdot}$, 219(75) $[C_4Br^{79}F_4O]^+$	15.9(16.0)	53.2(53.0)	25.5(25.4)
12a	C_4ClF_5O	40.0	1750	$194(27)M^{+\cdot}$, 147(100) $[C_3Cl^{35}F_4]^+$		18.1(18.2)	48.4(48.8)
12b	C_4BrF_5O	55.5	1740	$238(33)M^{+\cdot}$, 191(89) $[C_3Br^{79}F_4]^+$		33.3(33.4)	39.9(39.8)

a Parent ions and the most intense ions are quoted.
The chlorine and bromine isotope ions of characteristic relative intensities were present.

b X = Cl or Br, depends on the formula.

formamide or sulpholane gave 3-chloro-2,2,4,5,5-pentafluoro-2,5,dihydrofuran 12a and 3-bromo-2,2,4,5,5-pentafluoro-2,5-dihydrofuran 12b as virtually the only products; perfluoro-2,5-dihydrofuran was formed in less than a 1 % yield.



11a, 12a ; X = Cl
11b, 12b ; X = Br

Reaction of 11b with dry potassium fluoride in an autoclave at 290 - 300° also gave compound 12b, but in only 20% yield together with 45% recovery of starting material. The use of a higher reaction temperature led to carbonisation of the organic material.

^{19}F n.m.r. and mass spectra (Table 2 and 3) gave clear evidence for the structure of compounds 12a and 12b.

EXPERIMENTAL

Boiling points (uncorrected) were determined in a capillary. ^{1}H and ^{19}F n.m.r.spectra were recorded with a JEOL JNM-4H-100 spectrometer, and mass spectra were obtained with an Analytical GCMS System LKB-2091. 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 (GDR) using a 3.5 m x 0.4 cm column for analytical work and 4.0 m x 1.0 cm column for preparative work, both columns packed with Chromosorb G coated with 3% silicon oil SE-52.

2-(2-Chlorohexafluoropropyl)-pentachloro-2,5-dihydrofuran 2.

A solution of 2-(2H-hexafluoropropyl)-tetrahydrofuran 1 (26.6 g, 0.12 mole) in CCl_4 (15 ml) was placed in a three necked glass flask equipped with magnetic stirrer, reflux condenser and thermometer. The reactor was warmed to gentle reflux and then a slow stream of chlorine was introduced while irradiating by an external u.v. lamp. The chlorination was continued for 45 hours. During this time the reaction temperature was increased from an initial 70° to 210°. Distillation (105-106°/16 mmHg) gave 51.1 g (yield 99.8 %) of material identified as 2-(2-chlorohexafluoropropyl)-pentachloro-2,5-dihydrofuran 2.

Bromination of 2-(2H-hexafluoropropyl)-tetrahydrofuran 1.

A solution of bromine (25.3 g, 0.16 mole) in CCl_4 (10 ml) was added during 2 hours to an agitated solution of 2-(2H-hexafluoropropyl)-tetrahydrofuran 1 (13.3 g, 0.06 mole) in CCl_4 (10 ml) at 50 - 60°. The reaction mixture was refluxed for 20 hours and the reaction temperature was gradually increased to ca.150°. Distillation (boiling range 45 - 120°/ 10 mmHg) gave 18.8 g of oily material identified by g.l.c. - m.s. analysis as a mixture of bromofluorocompounds. Preparative g.l.c. separation allowed isolation of three shorter retention products, which were identified by spectral methods and elemental analysis (Table 2 and 3) as compounds 3,4,and 5.

Reactions of 2-(2-chlorohexafluoropropyl)-pentachloro-2,5-dihydrofuran 2 with potassium fluoride.

a) In aprotic solvents.

Compound 2 (5.1 g, 0.012 mole), diglyme or N,N-dimetylpyrrolidone (10 ml) and dry KF (8.1 g, 0.14 mole) were stirred together at 165 - 182° for 10 hours. A product and a part of the solvent were distilled off from the reaction mixture (boiling range 80 - 180°), diluted with water and the bottom organic layer was separated. This material (2.6 g) was shown by g.l.c. to contain 20% of the solvent and 80% of a single product. Preparative g.l.c. isolation gave a pure compound identified as 2-(2-chlorohexafluoropropyl)-3,4,5--trichlorofuran 6. Yield 49%. A similar run in diglyme without potassium fluoride also gave compound 6 as the only product.

b) In an autoclave without solvent.

A mixture of 2 (8.5 g, 0.02 mole) and freshly dried potassium fluoride (15 g, 0.26 mole) was placed in a 30 ml stainless steel autoclave and heated at 240 - 300° for 16 - - 25 hours. After completion of the reaction the contents of the autoclave were added to water and steam-distilled. The distillate was separated and the organic layer was dried over silica-gel and subjected to g.l.c. analysis. The results are summarized in Table 1. Preparative g.l.c. separation gave compounds 6 - 10, which were identified by spectral methods and elemental analysis (Table 2 and 3).

Synthesis of 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran 11a.

3,4-Dichloromaleic anhydride (455 g, 2.72 mole), anhydrous hydrogen fluoride (40 g, 2.0 mole) and sulphur tetrafluoride (760 g, 7.0 mole) were placed in a 2 l stainless steel rocking autoclave and heated at 200° for 24 hours. After completion of the reaction the reactor was allowed to cool to ambient temperature and then depressurized. The liquid reaction mixture was poured into iced water and neutralized by stirring for 2 hours with 10 % aqueous KOH and then washed with water and dried over $MgSO_4$ to give 224 g of raw material containing 95.3 % of compound 11a, 2.7 % of $CF_3CCl{=}CClCF_3$ and 2% other material. Yield 39 %. Distillation through 500 mm Fischer type column (Büchi) gave compound 11a of 99 % purity.

Synthesis of 3,4-dibromo-2,2,5,5-tetrafluoro-2,5-dihydrofuran 11b .

3,4-Dibromomaleic anhydride (500 g, 1.95 mole), anhydrous hydrogen fluoride (40 g, 2.0 mole) and sulphur tetrafluoride (600 g, 5.5 mole) were reacted at 200° for 24 hours. The reaction mixture was worked up as described above to give 375 g of raw material containing 77.6 % of compound 11b . G.l.c. yield 50 %. Distillation through a Fischer column gave compound 11b (240 g) of 95 % purity.

Reaction of 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran 11a with potassium fluoride.

The reaction was carried out in a 500 ml glass reactor equipped with a 0.5 m spiral distillation column and a cold finger type distillation head. The distillation head was kept at -10° using a 10 % aqueous ethanol-solid carbon dioxide mixture as cooling medium. The distillation head was connected to two receivers kept at -10° and -78°. The reactor was heated by means of an oil bath and its contents were stirred with a magnetic bar.

Dimethylformamide (200 ml), freshly dried KF (200 g), and compound 11a (105 g, 0.5 mole) were placed in the reactor and warmed slowly to 100°. At this temperature slow distillation occured and low boiling liquid was condensed in the receivers. After 4 hours at 100°, the reaction temperature was raised gradually during 3 hours to 150°. Combined distillate collected at -10° (68 g) and -78° (11 g) was shown by g.l.c. to consist of 3-chloro-2,2,4,5,5-pentafluoro-2,5--dihydrofuran 12a (63 %, g.l.c. yield 51.5 %) and unreacted 11a (37 %). Redistillation gave compound 12a (47 g) of 97 % purity.

Reaction of 3,4-dibromo-2,2,5,5-tetrafluoro-2,5-dihydrofuran 11b with potassium fluoride.

The reaction was carried out using apparatus as described above.

Dimethylformamide (150 ml), dried KF (100 g, 1.72 mole), and compound 11b (150 g, 0.5 mole) were heated at 120-130° (slow reflux) for 4 hours and then reaction temperature was gradually raised to 160°. A distillate collected in the first receiver (at 0°) was 3-bromo-2,2,4,5,5-pentafluoro-2,5-dihydrofuran 12b (80 g, yield 70.8 %) of 97 % purity.

A distillate (10 g) condensed in the second receiver (at -78°) was found by g.l.c.-m.s. to consist of compound 12b (66 %), $CF_3CBr{=}CFCF_3$ (28.5 %), and perfluoro-2,5-dihydrofuran (5.5 %).

A similar run using sulpholane as a solvent gave compound 12b in a 77.8 % yield and of 97.5 % purity.

REFERENCES

1 R.E.Banks, Fluorocarbons and Their Derivatives, MacDonald, London, (1970) Chapter 5.

2 W.J.Feast, W.K.R.Musgrave and N.Reeves, J.Chem.Soc. (C), (1971) 769.

3 R.Stroh, in Methoden der Organischen Chemie, Houben--Weyl, Bank 5/3, Stuttgart, (1962) p.609-611.

4 E.I. du Pont de Nemour and Co., Brit.Pat., (1949) 611.851; C.A., 43 (1949) 3041d.

5 G.Maas, Angew.Chem., Internat.Ed., 4 (1965) 787.

6 H.Muramutsu, K.Inukai and T.Ueda, Bull.Chem.Soc.Japan, 40 (1967) 903.

7 T.N.Abroskina, A.D.Sorokin, R.V.Kudryavtsev and I.A. Cheburkov, Izv.Akad.Nauk SSSR, Ser. Khim., (1974) 1823.

8 W.Dmowski, W.T.Flowers and R.N.Haszeldine, unpublished work, Manchester, (1976).

9 T.J.Batterham, N.m.r. Spectra of Simple Heterocycles, Wiley and Son, New York, (1973) Chapter 5/3, p.372.

10 T.Abe et all., J.Fluorine Chem., 12 (1978) 1, 359; 13 (1979) 519; 15 (1980) 353.

11 W.R.Hasek, W.C.Smith and V.A.Engelhardt, J.Am.Chem.Soc., 82 (1960) 543.

12 W.J.Feast, W.K.R.Musgrave and N.Reeves, J.Chem.Soc. (C), (1970) 2429.