Journal of Fluorine Chemistry, 20 (1982) 243–254

Received: June 26, 1981

POLYFLUORO-1,2-EPOXY-ALKANES AND -CYCLOALKANES. PART I. PREPARATION OF SOME POLYFLUORO-1,2-EPOXYCYCLOHEXANES

PAUL L. COE, ANDREW W. MOTT AND JOHN COLIN TATLOW

Chemistry Department, The University of Birmingham,
P.O. Box 363, Birmingham B15 2TT (Great Britain).

SUMMARY

Polyfluorocyclohexenes with hydrogen, bromine, and methoxy substituents yielded the corresponding 1,2-epoxides when treated with aqueous sodium hypochlorite containing some acetonitrile. 4,5-Dibromooctafluoro-1,2-epoxycyclohexane was debrominated with zinc dust to give a mixture of octafluoro- and 4H-heptafluoro-1,2-epoxycyclohex-4-ene. Decafluoro- and 4,5-dibromo-octafluoro-1,2-epoxycyclohexane gave with potassium fluoride in acetonitrile the corresponding potassium perhalogenocyclohexyloxides; heating these gave the analogous cyclohexanones, and treatment with methyl iodide the methyl ethers. The unsaturated 1,2-epoxides also gave methyl ethers on treatment with KF, followed by methylation.

INTRODUCTION

1,2-Epoxides are important and interesting synthetic intermediates in fluorocarbon chemistry [1], as they are in organic chemistry generally. Their ring-opening reactions [1] are utilized commercially to make [2] polymeric fluorocarbon polyethers. Higher fluorocarbon epoxides have been best made hitherto using alkaline hydrogen peroxide [3], an approach used [3,4] to make decafluoro-1,2-epoxycyclohexane (1) and thence decafluorocyclohexanone (9) via epoxy-ring-opening by attack with, and then loss of, fluoride ion [3,4]. We now describe a more convenient preparation of fluorocyclohexane-1,2-epoxides, together with some reactions of some of them.

0022-1139/82/0000-0000/$02.75

RESULTS AND DISCUSSION

We have found that the epoxidation of fluorocycloalkenes proceeds very conveniently using the method introduced by Kolenko, Filyakova, Zapevalov, and Lur'e [5], involving treatment with aqueous sodium hypochlorite in the presence of a polar co-solvent. For our epoxidations, acetonitrile was the preferred co-solvent. The fluorocyclohexenes used were made by a new modification of our heterogeneous dehydrofluorination process [6]. Table 1 records the details of the new fluorocyclohexane-1,2-epoxides made, Table 2 their special ir peaks, Table 3 their ^{19}F nmr peaks, and Table 4 the ^{1}H nmr peaks where applicable. All have nmr bands due to fluorine at the epoxidated carbon centres in the region 159-171 p.p.m. The epoxidation reaction did not work with 1-methyl- and 1-methoxy-nonafluorocyclohex-1-ene, both of which were recovered unchanged.

Decafluoro-1,2-epoxycyclohexane (1) was treated with potassium fluoride in acetonitrile and, after evaporation, potassium undecafluorocyclohexyl oxide (8) was left as a solid residue. This was quite stable if kept dry, but on being heated to around 200^{o} decomposed to decafluorocyclohexanone (9). This process is more convenient than our earlier reaction using KF/sulpholane [4], particularly for small scale work.

The alkoxide (8) reacted smoothly with methyl iodide in acetonitrile at 40^{o} to give methyl undecafluorocyclohexyl ether (10), known previously via fluorination of products of addition - elimination of sodium methoxide to decafluorocyclohexene [7].

Octafluorocyclohexa-1,3- and -1,4-diene [8] did not give epoxides on reaction with sodium hypochlorite/acetonitrile; complete oxidation to carboxylic acids occurred. However, the 4,5-dibromo-octafluoro-1,2-epoxycyclohexane (5), made from the dibromo-adduct of the 1,4-diene [8], reacted with zinc dust in n-propanol to give a mixture of the desired 1,2-epoxyoctafluorocyclohex-4-ene (11), together with (ratio 7:4) 1,2-epoxy-4H-heptafluorocyclohex-4-ene (12), presumably formed by solvent attack on an organometallic intermediate; 11 and 12 were separable by glc. Pyrolysis of the dibromo-epoxide (5) at 380^{o} left the oxygen ring intact, and gave the epoxy-ene (11), but only in poor conversion.

Each unsaturated 1,2-epoxide (11 and 12) was treated with KF in acetonitrile, and then with dimethylsulphate, to give methyl polyfluorocyclohexenyl ethers (14 and 15 respectively). The former (14) is the last remaining isomer of the methyl nonafluorocyclohexenyl ether series, the other two being known [7].

The dibromo-epoxide (5) with KF in acetonitrile gave a potassium alkoxide (16), which on heating gave 3,4-dibromooctafluorocyclohexanone (17), and with methyl iodide afforded 3,4-dibromo-1-methoxy-nonafluorocyclohexane (18).

1,2-Epoxyoctafluorocyclohexene (11) gave 4,5-dichloro-octafluoro-1,2-epoxycyclohexane (13) with chlorine under uv irradiation, the nmr spectrum indicating a 7:4 mixture of cis- and trans- chlorine addition products. Ring opening by KF, followed by heating the adduct gave 3,4-dichlorooctafluorocyclohexanone (19).

Thus, much useful synthetic chemistry is possible with polyfluorocyclohexane -1,2- epoxides, and further results will be reported later involving different nucleophiles for ring opening, and different epoxides.

EXPERIMENTAL

Spectroscopy Infrared spectra were recorded on a Perkin Elmer 257 instrument in the region 4000 - 625 cm^{-1} as liquid films (see Table 2).

^{19}F nmr spectra were recorded on a Perkin Elmer RB12 nmr spectrometer (^{1}H, 60 MHz; ^{19}F, 56.4 MHz). The results quoted in Table 3 for ^{19}F, are negative values measured from CCl_3F used as internal reference. Except where stated in Table 3 measurements were done on 20% solutions in $CDCl_3$. ^{1}H nmr spectra were recorded from tetramethylsilane as internal standard.

General Method of Preparation of Epoxides from Polyfluorocyclohexanes

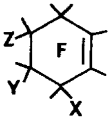
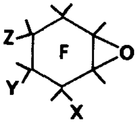
The cyclohexene (5g) was added during 15 min. to a vigorously - stirred mixture of acetonitrile (5 cm^3) and aqueous sodium hypochlorite solution (30 cm^3; M. and B. Laboratory Chemical, approx 12% available chlorine). The reaction mixture was warmed to 50° and stirred for 1h, water (50 cm^3) was then added, and the lower layer separated off, washed with aqueous sodium metabisulphite, then water, dried ($MgSO_4$), and distilled. Larger scale reactions were run with reactants in proportion, and for the same time. Results are recorded in Table 1. All compounds are new except decafluoro-1,2-epoxycyclohexane (1) [3,4,5].

Potassium Undecafluorocyclohexyloxide Decafluoro-1,2-epoxycyclohexane (1) (10.0g) and dry potassium fluoride (2.0g) in dry acetonitrile (30 cm^3) were stirred at 55° for 3h. Evaporation in vacuo yielded the white solid alkoxide (8) (10.1g) already reported [13].

Alkoxide (8) (3.0g) was heated at 200°/10 mm for 15 min, the product (2.4g) collected in a trap cooled to - 193° being decafluorocyclohexanone (9) [7,3,4] identified by i.r.

TABLE 1.

Preparation of Polyfluoro-1,2-epoxycyclohexanes

Starting Material			Product					Analysis					
								Found			Required		
Literature Reference	Derivative of Cyclohex-1,2-ene 	Weight (g)	Compound No.	Derivative of 1,2-epoxycyclohexane 	Yield (g)	Yield (%)	B.p. (°C)	C	H	F	C	H	F
[6,9]	X=Y=Z=F	100	(1)	X=Y=Z=F	87	82	54	25.7	-	-	25.9	-	-
[6,10]	X=H, Y=Z=F	5	(2)	X=H, Y=Z=F	3.5	67	68	27.4	0.4	65.5	27.7	0.4	65.8
[6,10]	Y=H, X=Z=F	5	(3)	Y=H, X=Z=F	3.8	73	73	27.2	0.3	66.1	ditto		
[6,11]	X=Y=H, 3H/4H; Z=F	16	(4)	X=Y=H, 3H/4H; Z=F	6.4	38	82	29.9	0.9	62.5	29.8	0.8	62.8
[8]	Y=Z=Br, X=F	175	(5)	Y=Z=Br, X=F	150	82	55-56 /8mm	18.0	40.2*	38.1	18.0	40.0*	38.0
[12]	Y=Br, X=Z=F	3.5	(6)	Y=Br, X=Z=F	2.1	56	103	21.0	23.5*	50.1	21.3	23.6*	50.4
[7]	X=OMe, Y=Z=F	3.0	(7)	X=OMe, Y=Z=F	2.2	69	109	29.2	0.7	59.0	29.0	1.0	59.0

*Br

Alkoxide (8) (3.0g) and methyl iodide (1.5g) in dry acetonitrile (20 cm^3) were stirred at 40^o for 5h, a white precipitate being formed. Water (100 cm^3) was added, the lower layer was separated and distilled to give methyl undecafluorocyclohexyl ether (10) [7] (1.4g), b.p. 100^o.

Debromination of 4,5-Dibromo-octafluoro-1,2-epoxycyclohexane (5)
(a) Using zinc dust. This epoxide (5) (30g) was added slowly to a stirred suspension of zinc dust (20g; activated by washing with dilute HCl, then water, and drying) in n-propanol (50 cm^3) at 60 - 70^o, the apparatus being swept with a nitrogen stream (2 l h^{-1}). After about ¼ of the epoxide had been added with no apparent effect, the reaction became vigorous and the rest was then added slowly. The volatile products were distilled out, washed with water, dried (P_2O_5) and separated by preparative glc (tube 4.8m x 35 mm packed with dinonyl phthalate/Chromosorb B 1:5, katharometer detector, 85^o, N_2 20 l h^{-1}) to give (i) 1,2-epoxyoctafluorocyclohex-4-ene (11) nc (7.1g) b.p. 57^o (Found: C, 30.0. C_6F_8O requires C, 30.0%); and (ii) 1,2-epoxy-4H-heptafluorocyclohex-4-ene (12) nc (4.2g) b.p. 68^o (Found: C, 32.6; H, 0.5; F, 59.6. C_6HF_7O requires C, 32.4; H, 0.5; F, 59.9%).
(b) On pyrolysis. Epoxide (5) (3.0g) was passed during 30 min. in a stream of nitrogen (1 l h^{-1}) through a vertical column (500 mm x 30 mm made of Pyrex glass and packed with 25 mm lengths of small-bore Pyrex tubing) at 380^o. The product (1.6g) was trapped at - 193^o, washed with sodium metabisulphite solution and water. Separation by glc as above (N_2,10 l h^{-1}) gave product (11) (22%), and starting material (5) (78%).

4,5-Dichloro-octafluoro-1,2-epoxycyclohexane (13) The epoxy-ene (11) (5.0g) and chlorine (2.0g) were sealed in a 300 mm Carius tube which was irradiated with ultraviolet light for 15 h. The product was washed with sodium metabisulphite solution, then water and distilled off P_2O_5 to give the epoxydichloride (13) nc (4.5g) b.p. 118^o (Found: C, 23.2; Cl, 22.8; F, 48.8. $C_6Cl_2F_8O$ requires C, 23.2; Cl, 22.8; F, 48.9%).

4-Methoxynonafluorocyclohex-1-ene (14) Expoxy-ene (11) (1.1g) was stirred with dry potassium fluoride (0.4g) in dry acetonitrile (5 cm^3) at 50^o for 2h. Dimethyl sulphate (1.5g) was then added and the mixture stirred at 50^o for 2h further. Water (10 cm^3) was added, the organic layer washed with dilute KOH solution, then water, and distilled from P_2O_5 to give 4-methoxynonafluorocyclohex-1-ene (14) nc (0.4g) (Found: C, 30.4; H, 0.6. $C_7H_3F_9O$ requires C, 30.7; H, 1.1%).

Methoxyoctafluorocyclohexene (15) The 4H-epoxy-ene (12) (1.0g) and dry potassium fluoride (0.4g) in dry acetonitrile (5 cm^3) were stirred at 50^o for 4h. Dimethyl sulphate (1.5g) was added and stirring continued at 50^o for 2h. Water was added, the fluorocarbon layer washed with dilute aqueous KOH, then water,dried and distilled in vacuo. The mixture was separated by glc (Pye 104, tube 9.1m x 7mm packed with dinonyl phthalate/Celite 1:2, 75^o, N_2 3 l h^{-1}) to give starting material (12) (0.2g) and 1H-4-or -5-methoxyoctafluorocyclohex-1-ene (15) nc (0.4g) b.p. 121^o (Found: C, 32.7; H, 1.6. $C_7H_4F_8O$ requires C, 32.8; H, 1.6%).

Reactions of Potassium 3,4-Dibromononafluorocyclohexyloxide (16) Dibromo-epoxide (5) (5.0g) was stirred with dry potassium fluoride (1.0g) in dry acetonitrile (30 cm^3) for 3h at 80^o. Evaporation of the solvent at 17^o/5mm left a solid alkoxide (16) (5.5g).

A portion (3.0g) of (16) was heated at 200^o/10mm and the volatile product trapped at - 193^o. Distillation from P_2O_5 afforded 3,4-dibromo-octafluorocyclohexanone (17) nc (1.8g) b.p. 187^o (Found: C, 18.2; Br, 39.9; F, 38.5. $C_6Br_2F_8O$ requires C, 18.0; Br, 40.0; F, 38.0%).

Cyclohexyloxide (16) (4.0g) and methyl iodide (3.0g) in dry 1,2-dimethoxyethane (10 cm^3) were stirred at 15^o for 4h. Water (30 cm^3) was added, the organic layer was washed with water, dried ($MgSO_4$), and distilled in vacuo to give 3,4-dibromo-1-methoxynonafluorocyclohexane (18) nc (2.4g) b.p. 182^o (Found: C, 19.5; H, 0.5. $C_7H_3Br_2F_9O$ requires C, 19.4; H, 0.7%).

3,4-Dichloro-octafluorocyclohexanone (19) Treatment of the dichloro epoxide (13) (3.0g) in the same way as the dibromo-analogue (above) gave the potassium alkoxide which on heating afforded 3,4-dichloro-octafluorocyclohexanone (19) nc (2.5g) b.p. 150 - 152^o (Found: C, 22.6; Cl, 22.5; F, 48.7. $C_6Cl_2F_8O$ requires C, 23.2; Cl, 22.8; F, 48.9%).

Reactions of Octafluorocyclohexadienes with Aqueous Sodium Hypochlorite When octafluorocyclohexa-1,3-diene (5.0g) was treated according to the standard procedure there was no fluorocarbon layer. The solution was acidified, extracted with ether and S-benzyl thiouronium chloride added to the extract in the normal way to give the known [8] salt of tetrafluorosuccinic acid (2.0g). The octafluoro-1,4-diene (3.0g) similarly gave the salt [8] of difluoromalonic acid (1.4g).

TABLE 2

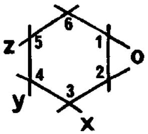
Key Infrared absorptions of 1,2-epoxides and Compounds Derived Therefrom

Compound Number		1	2	3	4	5	6	7
Frequency (cm^{-1}) of bands from:-	$\overset{O}{\overset{/\backslash}{C\text{-}C}}$	1490	1487	1480	1480	1490	1482	1475
	C-H	-	2962	2970	2960	-	-	2960

Compound Number		11	12	13	14	15	17	18	19
	$\overset{O}{\overset{/\backslash}{C\text{-}C}}$	1495	1491	1488	-	-	-	-	-
Frequency cm^{-1}	C-H	-	(3070 (3100	-	(2870 (2920 (2970	(2870 (2980 (3010 (3100	-	(2868 (2973 (3020	-
	C=C	1740	1710	-	1743	1710	-	-	-
	C=O	-	-	-	-	-	1800	-	1800

TABLE 3

^{19}F n.m.r. Spectra

Compound No.		Peaks Chemical Shift	Relative Intensity	Coupling	Assignment
2	X=H, Y=Z=F	159.2	1	t, J = 19	1
		168.3	1	m	2
		212.7	1	dm, J = 50	3
		127.2	2	cAB, J = 288, $\Delta\nu$ = 419	4,5,6
		127.6	2	cd, J = 257	
		134.3	2	cs	
3	Y=H, X=Z=F	167.9	2	m	1,2
		225.9	1	dm, J = 48	4
		121.1	2	m	3,5,6
		126.9	1	m	
		128.4	1	m	
		129.3	2	m	
4	X=Y=H, Z=F (94 MHz)	168.5	1	cs	1
		170.7	1	cs	2
		217.9	1	cd, J=50	3
		219.7	1	cd, J=45	4
		119.7	2	cAB, J=270, $\Delta\nu$=1589	5,6
		123.6	2	cs	

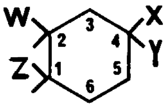
5	Y=Z=Br, X=F	163.5	1	cm	1,2
		166.1	1	cm	
		129.2	1	cm	4,5
		131.6	1	cm	
		109.3	2	AB, J=262, Δν=756 Am; Bct, J=14	3,6
		110.2	2	AB, J=277, Δν=1243 Adt, Jd=10, Jt=24 Bt, J=14	
6	Y=Br, X=Z=F	162.7 - 169.0	2	4 complex peaks	1,2
		100.1 - 140.5	7	c	3,4,5,6
7	X=OMe, Y=Z=F	167.9	1 0.6	cs	1
		169.0	0.4	cs	
		159.2	1 0.6	ct, J=19	2
		163.5	0.4	cd, J=25	
		118.1 -139.1	7	complex series of peaks	3,4,5,6
11	X=F, Y and Z are FC=CF	175.2	1	m	1,2
		154.2	1	m	4,5
		117.4	2	cAB, J=296, Δν=823	3,6

b = broad, c = complex, d = doublet, m = multiplet, q = quartet, s = singlet, t = triplet

(continued overleaf)

TABLE 3 (cont.)

Compound No.		Peaks			
		Chemical Shift	Relative Intensity	Coupling	Assignment
12	X=F, Y and Z are FC=CH	175.5	1	cm	1,2
		176.4	1	cm	
		123.4	1	cm	5
		110.0	1	cm	3,6
		115.4	1	tcm, Jt=20	
		113.5	2	cAB, J=301, Δν=1416	
13	Y=Z=Cl, X=F major isomer	164.4	1	cm	1,2
		166.9	1	cm	
		128.5	1	cq, J=12	4,5
		134.7	1	cd, J=9	
		114.8	2	cAB, J=270, Δν=747	3,6
		115.4	2	cAB, J=267, Δν=951	
	minor isomer	165.4	1	cm	1,2
		130.5	1	cm	4,5
		115.8	2	cAB, J=280, Δν=1208	3,6



14	X=OMe, Y=F	145.0	1	cs	4
	W and Z are FC=CF	156.1	2	cm	1,2
	(neat)	117.6	2	cd, J=113	
		127.1	2	cAB, J=288, Δν=1210	3,5,6
		127.6	2	cd, J=288	
15	X=OMe, Y=F	136.3	1	cs	4
	W and Z are	145.0	1	cs	1 or 2
	FC=CH	109.2	2	cAB, J=290, Δν514	
	(neat)	118.9	2	cd, J=125	3,5,6
		127.6	2	cd, J=276	
17	X and Y C=O	96.7	-	complex series	-
	W=Z=Br	-140.7		of peaks	
18	X=OMe, Y=F,	138.2	1	cs	4
	W=Z=Br	126.5	2	cm	1,2
		111.2	2	cAB, J=287, Δν=955	
		120.5	2	cAB, J=276, Δν=1258	3,5,6
		123.3	2	cd, J=125	
19	X and Y C=O	102.3	-	complex series	-
	W=Z=Cl	-141.7		of peaks	

TABLE 4

Proton n.m.r. Spectra

Compound No.	Chemical Shift	Relative Intensity	Coupling	Assignment
2	5.1	-	cd, J=49	3H
3	4.8	-	dq, Jd=45, Jq=9	4H
4	4.83	-	dm, J=53	3H/4H
7	3.80	-	cs	$-OCH_3$
12	5.85	-	11 peaks, J≈7	4H
14	3.60	-	cs	$-OCH_3$
15	3.57 5.65	3 1	cs bm	$-OCH_3$ 1H
18	3.8	-	cs	$-OCH_3$

REFERENCES

1 P. Tarrant, C.G. Allison, K.P. Barthold, and E.C. Stump, Fluorine Chem. Reviews, 5 (1971) 77.

2 Inter alia, J.L. Warnell,U.S.P. 3,250,806 (1966); E.P. Moore, U.S.P. 3322826 (1967); C.G. Fritz and E.P. Moore, U.S.P. 3250807 (1966); (all to DuPont Co.).

3 E.P. Moore and A.S. Milian, B.P. 1,019,788 (1966).

4 P.L. Coe, J.H. Sleigh, and J.C. Tatlow, J. Fluorine Chem., 15 (1980) 339.

5 I.P. Kolenko, T.I. Filyakova, A. Ya. Zapevalov, and E.P. Lur'e , Izvest. Akad. Nauk. S.S.S.R., Ser.Khim., (1979) 2509: U.S.S.R. Patent 666176 (1979).

6 P.L. Coe, A.W. Mott, and J.C. Tatlow, J. Fluorine Chem. 20 (1982) 167.

7 A.B. Clayton, R. Stephens, and J.C. Tatlow, J. Chem. Soc., (1965) 7370: A.B. Clayton, J. Roylance, D.R. Sayers, R. Stephens, and J.C. Tatlow, ibid. p. 7358.

8 D.E.M. Evans and J.C. Tatlow, J. Chem. Soc., (1954) 3779.

9 J.C. Tatlow and R.E. Worthington, J. Chem. Soc., (1952) 1251: A.K. Barbour, H.D. Mackenzie, M. Stacey, and J.C. Tatlow, J. Appl. Chem., 4 (1954) 347.

10 D.E.M. Evans and J.C. Tatlow, J. Chem. Soc., (1955) 1184.

11 J.A. Godsell, M. Stacey, and J.C. Tatlow, Tetrahedron, 2 (1958) 193.

12 T.W. Bastock, M.E. Harley, A.E. Pedler, and J.C. Tatlow, J. Fluorine Chem., 6 (1975) 331.

13 L.G. Anello, A.K. Price,and R.F. Sweeney, J. Org. Chem., 33 (1968) 2692.