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POLYFLUORO-1,2-EPOXY-ALKANES AND -CYCLOALKANES. PART III. SOME 1,2-EPOXIDES DERIVED FROM OLIGOMERS OF TETRAFLUOROETHYLENE

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SUMMARY

Three oligomers ($[R_1][R_2]C{=}C[R_3][F]$) of tetrafluoroethylene, the trimer ($R_1 = C_2F_5$-; $R_2 = R_3 = CF_3$-), the pentamer ($R_1 = (C_2F_5)_2(CF_3)C$-; $R_2 = R_3 = CF_3$-) and the major hexamer isomer ($R_1 = (C_2F_5)_2(CF_3)C$-; $R_2 = (C_2F_5)(CF_3)(F)C$-; $R_3 = F$) reacted with aqueous sodium hypochlorite/ acetonitrile to give high yields of the corresponding 1,2-epoxides. Perfluoro-1-methyl-2-(1-methylpropyl)cyclobutene (derived from the hexamer by pyrolysis) and perfluoro-4-ethyl-2,3,4,5-tetramethyl-4,5-dihydrofuran (made by hydrolysis of the pentamer) also underwent efficient epoxidation. The epoxy-oxolan decomposed in two ways at 280-480°C, one process giving the trimer of tetrafluoroethylene, probably by a radical pathway, and the other process, involving fluoride ion, affording tetradecafluoro-3,4-dimethylhex-3-ene-2-one.

INTRODUCTION

Decafluoro-1,2-epoxycyclohexane [1] resembles other fluoro-epoxides [2] in being a valuable synthetic intermediate. We found that, together with other polyfluoro-1,2-epoxycyclohexanes [3], it can be made very conveniently by direct epoxidation of the corresponding fluorocyclohexene, using aqueous sodium hypochlorite and acetonitrile, following a process introduced first by Kolenko and co-workers [4]. We extended this further, to the epoxidation [5], of perfluoro-[(1-ethyl-1-methylpropyl)(1-methylpropyl)] keten, readily obtained by alkaline hydrolysis of the major hexamer isomer of tetrafluoroethylene (III; see Scheme). This gave us perfluoro-[1-ethyl-1-methylpropyl)·(1-methylpropyl)]-ethanolide, not only the first α-lactone to be made by direct oxygenation, but also the most stable obtained so far [5].

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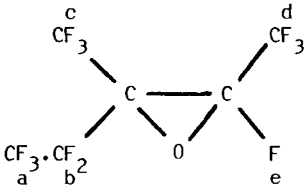
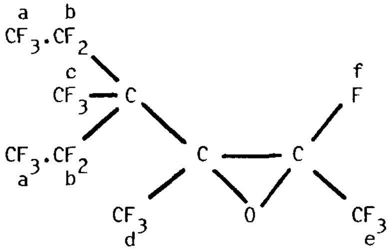
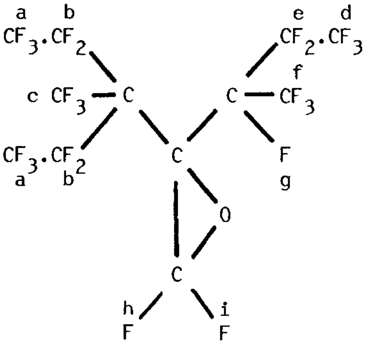


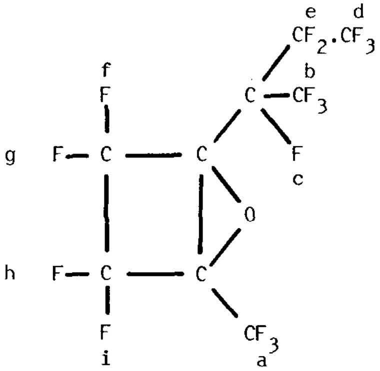
Iα (E-isomer)



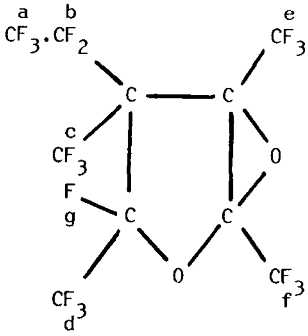
IIα



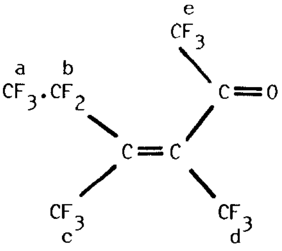
IIIα



IVα



Vα



VI (Z-isomer)

SCHEME

ALKENE STARTING MATERIALS (I to V) CORRESPOND TO EPOXIDE PRODUCTS (Iα to Vα) WITH DOUBLE BONDS IN PLACE OF OXIRANE RINGS

We next tried the direct epoxidation of the trimer (I), pentamer (II) and major hexamer (III) of tetrafluoroethylene, oligomers obtained readily by anionic polymerisation [6]. A cyclobutene (IV) derived from the hexamer by pyrolysis [7] and an oxolen (V) derived from the pentamer, were also included in the study. This paper describes these results, and also experiments on the pyrolytic decomposition of the epoxy-oxolan (Vα).

RESULTS AND DISCUSSION

Synthesis of epoxides

The short-chain oligomers of tetrafluoroethylene are highly branched perfluoro-olefins, with reagent approach to their double bonds hindered by bulky groups. Nevertheless, epoxidation with aqueous sodium hypochlorite/ acetonitrile proceeded readily, and high yields of products resulted even in large-scale experiments (see Table 1). Each product had a correct analysis, and an ir band due to the oxirane ring at 1400-1500 cm^{-1}.

The trimer (I) is a mixture of E (90%) and Z (10%) stereoisomers, and its epoxide (Iα) should exist as two diastereoisomeric pairs of enantiomers. Compound (Iα) was a mixture of E (65%) and Z (35%) forms, as shown by ^{19}F nmr. Though all peaks were complex multiplets, in the E-form, coupling between the cis-CF_3 groups carried on the epoxy-ring gave a quartet for C1 (position d), whilst the Z-form had a quartet for the only isolated fluorine (position e), coupled with the cis-arranged CF_3 carried on C3. The difference in ratio of the respective E and Z structure forms shows that the epoxidation of an acyclic olefin is not stereospecific, and that rotation of groups around an incipient single bond is possible, before the ring is established.

Tetrafluoroethylene pentamer (II) is entirely the E-form, the 'trident' group $[(C_2F_5)_2CCF_3]$ being preferentially cis to the vinylic fluorine. The derived epoxide (IIα) is also the (presumably racemic) E-stereoisomer only (^{19}F nmr; quartet at position e, coupled with the cis-CF_3; doublet coupling at positions a to the cis-disposed tertiary fluorine). Here, the bulky trident group hinders any molecular rearrangement.

The major hexamer isomer (III) is a racemate (chiral centre at C_3), but after epoxidations there are chiral centres at positions 2 and 3 in the epoxide (IIIα), which should therefore exist as two enantiomeric pairs.

This was shown up in the ^{19}F nmr spectrum, there being two signals for CF_3 at position a, and two for CF_2 at position b, indicating that two forms were present in equal proportion.

When the hexamer (III) is pyrolysed [7], preferential bond-breaking within the trident group gives rise to a perfluorobuta-1,3-diene, which in turn cyclises at the temperatures involved, and gives rise to a cyclobutene (IV) (a racemate), as the major product. Epoxidation of IV gave the first example of a perfluorocyclobutane-1,2-epoxide (IVα). This has three chiral centres but, because of the ring structure, exists as two enantiomeric pairs. The ^{19}F nmr spectrum showed the presence of two such forms (ratio 2:1), since there were two distinct peaks due to the CF_3 group at position b. There was obviously a preferred side of approach for the reagent to the double bond.

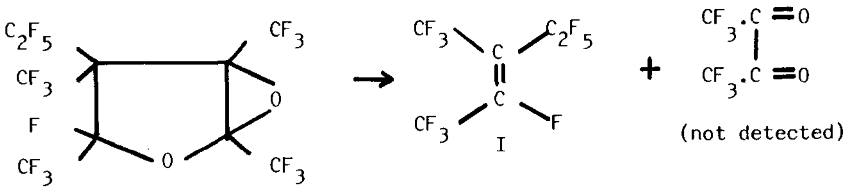
Treatment [8] of the pentamer (II) with triethylamine and water at low temperature affords the oxolen (V) in good yield. Although there is the possibility of two diastereoisomeric systems, the ^{19}F nmr evidence suggested that the product consisted predominantly (>95%) of one of them, presumably a pair of enantiomers. Epoxidation of oxolen (V) proceeded quite readily, and the epoxy-oxolan (Vα) showed two closely-related forms in the ratio 3:1 (different ^{19}F nmr peak positions for all groups but one). Clearly the original oxolen enantiomeric pair was epoxidated in both possible ways to give the expected two pairs of enantiomeric epoxides. Again, one side of the molecule offered an easier approach for the reagent.

Decomposition of the epoxy-oxolan (Vα)

It was thought that these epoxides (Iα-Vα) might decompose readily at quite low temperatures [cf. 2]. This was not the case however; all were relatively stable to heat. Pyrolytic decomposition of the oxolan-epoxide (Vα) was studied in some detail. Over a packing of hard glass, little happened below 300°C. At higher temperatures (Table 2), two liquid products were formed, besides gaseous fragments. One was tetrafluoroethylene trimer (I), and the other a new unsaturated ketone (VI). This analysed as $C_8F_{14}O$, and ^{19}F nmr spectroscopy showed the structure to be tetradecafluoro-3,4-dimethylhex-3-ene-2-one (VI). Z and E forms were present, with the E in slight excess, and were separated by glc.

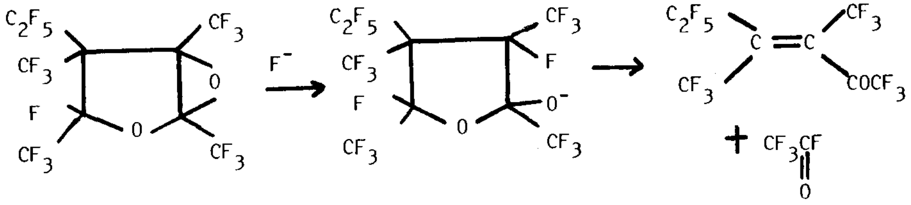
Further investigation of the decomposition of the oxolan-epoxide (Vα) (Table 2) showed that at temperatures from 310-350°C, trimer I was the major product. At 400°C, ketone VI predominated, but, by 480°C, trimer I again was the major product. However, over a mixed packing of glass fragments and sodium fluoride, the decomposition proceeded rather more readily. By 280°C, nearly 50% of Vα had decomposed, largely to VI with very little I; at 330°C, VI was still the major product, but more I was present.

It seemed that two distinct reactions were occurring simultaneously. One, it is suggested, was free-radical in nature, and proceeded preferentially at lower temperatures, and in the absence of fluoride ion (Pathway 1). It involved breaking of the carbon-carbon bond between the most substituted carbons, a well-recognised reaction in this area [cf. 7], together with a carbon-oxygen bond:-



PATHWAY 1

The other process (Pathway 2) was promoted by fluoride ion, and ring-opening of an oxirane function by fluoride ion is one of the most important



PATHWAY 2

reactions of fluorocarbon epoxides [2]. If it is accepted that fluoride ion attack occurs in the direction indicated, and that trifluoroacetyl fluoride is eliminated from the derived alkoxide, the α β-unsaturated ketone (VI) would be formed. The gaseous products had infrared bands corresponding to the reported carbonyl peaks for carbonyl fluoride and trifluoroacetyl fluoride.

It seems that, in the absence of a fluoride packing, at 300-350^{o}C pathway 1 predominated (compare the breaking of a quarternary-tertiary C-C bond in a fluorocarbon at just over 300^{o}C [7]). At 350-450^{o}C, the fluoride-ion-promoted process (pathway 2) became predominant. However, at temperatures over 400^{o}C, the product of pathway 2, the oct-ene-one (VI), decomposed increasingly rapidly relative to the trimer. Thus, by 480^{o}C trimer I again was the major product, but total recoveries were poor.

This hypothesis was supported by the copyrolysis of a mixture of the enone (VI) and the trimer (I) at 480^{o}. The starting material had an VI/I ratio of 1.3:1, and the VI/I ratio of the product was 1:15, indicating that thermal decomposition of the ketone (VI) is much faster than that of the trimer (I) at the temperature of the experiment.

In the presence of a fluoride packing, pathway 2 was speeded up, and ketone VI was the major product, though the thermal process (pathway 1) was still operating, and some trimer (I) was formed.

EXPERIMENTAL

Nuclear magnetic resonance (^{19}F) Measurements were on a Perkin Elmer R12B machine at 56.4 MHz, on neat samples, using trichlorofluoromethane as internal reference. Except where stated, all peaks were complex multiplets: c = complex, d = doublet, q = quartet, AB = AB quartet (mid-point position quoted), s = sextuplet, sp = septet. Values recorded are δ units, and are actually negative; positions in skeletons are indicated by the small letters on the formulae in the Scheme. Results are given in Table 3.

General Method for Epoxidation of Perfluoro-olefins The olefin was added carefully to a vigorously-stirred mixture of aqueous sodium hypochlorite (M. and B. Laboratory Chemical; approx. 12% available chlorine) and ethanonitrile (acetonitrile). There was usually some evolution of heat. After the reaction, the fluorocarbon layer was separated, washed with water, dried (P_2O_5) and distilled. Details are given in Table 1.

Perfluoro-3-methylpent-2-ene (trimer) (I) gave perfluoro-3-methyl-2,3-epoxypentane (Iα) nc.

Perfluoro-4-ethyl-3,4-dimethylhex-2-ene (pentamer) (II) in the large-scale run gave a crude fluorocarbon layer, which was washed with water, 10% sodium metabisulphite solution, water again, and was dried (P_2O_5) (810 g) to give, by distillation, the E-isomer of perfluoro-4-ethyl-3,4-dimethyl-2,3-epoxyhexane (IIα) nc.

TABLE 1

Epoxidation of Perfluoro-olefins

Starting Material			Reaction Conditions				Product		
Compound Reference	Literature Reference	Weight (g)	NaOCl (cm^3)	CH_3CN (cm^3)	Temperature (°C)	Time (hours)	Compound Reference (See Scheme)	Weight (g)	Boiling Point (°C)
I	[6]	10.0	100	30	18	1	Iα	7.0	47
II	[6]	40	180	120	18	5	IIα	39	147-148
II	[6]	800	1000	250	18	3	IIα	740	146-147
III	[6]	50	225	150	18	2	IIIα	49.6	186
IV	[7]	7.2	40	15	25	½	IVα	4.0	110
V	[8]	200	450	150	45	3	Vα	165	138-139

Product	ir (cm^{-1})	Formula	Analysis			
			Found		Required	
			C %	F %	C %	F %
Iα	1460	$C_6F_{12}O$	22.6	-	22.8	-
IIα	1410	$C_{10}F_{20}O$	23.0	73.7	23.3	73.6
IIIα	1450	$C_{12}F_{24}O$	23.1	74.3	23.4	74.0
IVα	1480	$C_9F_{16}O$	24.6	71.2	25.2	71.0
Vα	1485 1495	$C_{10}F_{18}O_2$	24.0	69.4	24.3	69.2

Perfluoro-2-(1-ethyl-1-methylpropyl)-3-methylpent-1-ene (major hexamer isomer) (III) afforded perfluoro-2-(1-ethyl-1-methylpropyl)-3-methyl-1,2-epoxypentane (IIIα) nc.

Perfluoro-1-methyl-2-(1-methylpropyl)cyclobut-1-ene (IV) gave perfluoro-1-methyl-2-(1-methylpropyl)-1,2-epoxycyclobutane (IVα) nc.

Perfluoro-4-ethyl-2,3,4,5-tetramethyloxal-2-en (V) gave a crude product (199 g; after being dried over calcium chloride). Distillation at reduced pressure, through a 30 cm vacuum-jacketed column packed with glass helices, gave a fraction, b.p. 56-57°/30 mm Hg, which was perfluoro-4-ethyl-2,3,4,5-tetramethyl-2,3-epoxy-oxolan (Vα) nc: Found, m/e 494 (M), 475 (M-F), 456 ($M-F_2$), 425 ($M-CF_3$).

Pyrolyses of Epoxy-oxolan (Vα) Experiments were done in Pyrex glass tubes (75 cm x 2 cm int. diam.) mounted vertically, and heated electrically. Packings were short lengths of small bore Pyrex glass tubing (2 cm x 0.5 cm int. diam.) (Tube A), and the same mixed with coarse sodium fluoride powder (3:4 by weight) (Tube B). The tubes were conditioned by passage of dry benzene (400 cm^3) at 300°C.

In a typical run to determine product composition (see Table 2) epoxy-oxolan (Vα) (10.0 g) was dripped during 2 h into the pyrolysis tube in a stream of nitrogen (2 lh^{-1}), products being held in a trap cooled to -178°C. The tube was swept with nitrogen (5 lh^{-1}) for ½ h (Tube A) or 1 h (Tube B). Liquid products were assayed by glc (3 m column packed with 2 m di(2-cyanoethyl) ether/Poracil C (1:5) and 1 m dinonylphthalate/Celite (1:5); temp. 70°C; N_2 overpressure 10 p.s.i.; Pye 104 machine with a flame ionisation detector; calibrations by measurements on known mixtures). Results are given in Table 2.

A large scale experiment was done using Vα (100 g) passed through tube A at 400°C during 10 h. The product, after gaseous material had been allowed to evaporate (66.2 g), was distilled through a 15 cm column packed with glass helices to give:- (i), (6.1 g) b.p. 24-53°C, I (55%) + unknown (45%): (ii), (12.3 g) b.p. 53°C (I): (iii), (9.4 g) b.p. 53-86°, I (27%) + VI (73%): (iv), (34.2 g) b.p. 86-90°, VI (96%) + I (2%) + Vα(2%): (v) (4.7 g) still residue, Vα (80%) + unknown (20%). Fraction (ii), perfluoro-3-methylpent-2-ene (I), had an ir band at 1685 cm^{-1} (C=C).

Fraction (iv), after purification by glc, afforded tetradecafluoro-3,4-dimethylhex-3-ene-2-one (VI) nc: b.p. 88-89°C(Found: C, 25.1; F, 70.8. $C_8F_{14}O$ requires C, 25.4; F, 70.4%): m/e 359 (M-F), 309 (M-CF_3), 259 (M-C_2F_5): ir 1770 cm^{-1} (C=O) (no obvious band for C=C). Compound VI (250 mg), on further glc (column A [7], 65°, N_2 1 lh^{-1}), gave (iv) a, the E-stereoisomer (110 mg): (iv) b, the Z-stereoisomer (95 mg).

A sample (10 g) of trimer (I) + eneone (VI) (43:57 molar %) was passed in a stream of nitrogen (2 lh^{-1}) through tube A at 480°C during 2 hours. After passage of nitrogen for 30 min. further, the non-gaseous products (4.05 g), by glc analysis, contained I + VI in ratio 94:6 molar %. About 50% of trimer (I) was recovered, but only ca. 2% hexenone (VI). There were some six minor peaks on glc due to decomposition products.

ACKNOWLEDGEMENTS

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TABLE 2

Thermal Decomposition of the Epoxy-oxolan (Vα)

Tube	Temperature (°C)	Recovery (% by wt.)	Product Mixture (Molar %)			Ratio I:VI (%)
			Vα	I	VI	
A	310	95	80	20	0	100:0
A	350	84	6	82	12	87:13
A	400	68	5	35	60	37:63
A	450	47	3	41	56	42:58
A	480	36	0	72	28	72:28
B	280	72	52	2	46	4:96
B	330	63	9	23	69	25:75

TABLE 3

^{19}F nmr Spectra

Compound Number	Chemical Shift	Relative Intensity	Position in Formula (see Scheme)	Type of Signal and Coupling
I	60.0	3	c	c
E-isomer	70.1	3	d	q, J=17
(90%)	87.7	3	a	cd, Jd=14
(external	96.3	1	e	c
CCl_3F)	114.6	2	b	dq, Jd=28, Jq=14
Z-isomer	61.1	3	c	c
(10%)	69.5	3	d	c
(external	86.2	3	a	c
CCl_3F)	93.2	1	e	c
	110.1	2	b	c
Iα	65.1	3	c	c
E-isomer	73.1	3	d	q, J=12.5
(65%)	81.2	3	a	c
	113.2	2	b	cAB
	146.7	1	e	c
Z-isomer	65.9	3	c	c
(35%)	73.4	3	d	c
	81.2	3	a	c
	113.2	2	b	cAB
	149.0	1	e	q J=22.5
IIα	53.1	3	c	c
	61.0	3	d	c
	72.3	3	e	q, J=18.0
	77.3	6	a	cd, J=48
	100.4	4	b	c
	141.0	1	f	c

Table 3 (cont.)

Compound Number	Chemical Shift	Relative Intensity	Position in Formula (see Scheme)	Type of Signal and Coupling
IIIα	53.3	3	c	c
	69.3	3	f	c
	75.4, 76.8	3,3	a	c
	79.5	3	d	c
	92.3	1	i	c
	96.1, 98.5	2,2	b	c
	104.5	1	h	c
	110.2	2	e	cAB
	169.4	1	g	c
IVα	66.1	3	a	c
	72.2, 73.6	1,2	b	c
	80.6	3	d	c
	115.8 118.1 119.4 121.7 125.7 129.2	6	e f g h i	c
	185.5	1	c	c
Vα major isomer (75%)	59.7	3	c	c
	61.4	3	e	c
	72.7	3	f	q, J=9.0
	76.6	3	a	s, J=14
	78.8	3	d	dq, Jd=45, Jq=7.5
	102.5	1	g	cq, Jq=45
	106.0	2	b	c
Vα minor isomer (25%)	56.2	3	c	c
	57.3	3	e	c
	71.9	3	f	q, J=10.3
	76.6	3	a	s, J=14.1

(cont. overleaf)

Table 3 (cont.)

Compound Number	Chemical Shift	Relative Intensity	Position in Formula (see Scheme)	Type of Signal and Coupling
	76.8	3	d	c
	100.3	2	b	c
	109.5	1	g	c
VI E-isomer (external CCl_3F)	56.3	3	c	c
	57.5	3	d	c
	76.0	3	e	c
	80.7	3	a	sp, J=7.5
	109.1	2	b	c
Z-isomer (external CCl_3F)	59.0	3	d	c
	59.5	3	c	c
	78.4	3	e	c
	84.4	3	a	q, J=7.5
	107.5	2	b	c

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