Journal of Fluorine Chemistry, *27* (1985) 71–84

Received: May 23, 1984; accepted: June 22, 1984

POLYFLUORO-1,2-EPOXY ALKANES AND CYCLOALKANES. PART IV [1]. THERMAL REACTIONS OF THE EPOXIDES OF THE PENTAMER AND HEXAMER OLIGOMERS OF TETRAFLUOROETHENE

P.L. COE*, A. SELLARS, J.C. TATLOW

Chemistry Department, University of Birmingham, P.O. Box 363,
Birmingham B15 2TT (U.K.)

H.C. FIELDING and G. WHITTAKER

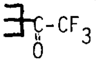
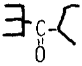
ICI PLC, Mond Division, The Heath, Runcorn, Cheshire (U.K.)

SUMMARY

Oxirans (1) and (2), derived respectively from the pentamer and hexamer oligomers of tetrafluoroethene, were pyrolysed over pyrex glass at 300-500° alone and in the presence of cyclohexene, bromine and toluene. Thus, oxiran (1), pyrolysed alone, afforded perfluoro-2-methylbut-1-ene (3), perfluoro-2,3-dimethylpent-2-ene (4) and (E) and (Z) perfluoro-2,3-hex-3-ene (TFE tetramer) (5a, 5b). Co-pyrolysis of (1) with bromine afforded (E) and (Z) 2-bromoperfluoro-3-methylpent-2-ene (6a, 6b), whilst with toluene, (E) and (Z) 2H-perfluoro-3-methylpent-2-ene (7a, 7b) were obtained: (1) with excess cyclohexene also gave (7a, 7b). The oxiran (2), on pyrolysis alone, gave only (3). In the presence of bromine, (2) gave an equimolar mixture of 1-bromoperfluoro-3-methylpentan-2-one (8) and 3-bromoperfluoro-3-methylpentane (9). Co-pyrolysis of (2) with toluene yielded (3) and 3H-perfluoro-3-methylpentane (10). Pyrolysis of (2) with cyclohexene at 175° gave perfluoro-3-methyl-2-(1-methylpropyl)pent-2-en-1-oylfluoride (11), pentafluoroethylcyclohexane (12) and perfluoro[(1-ethyl-1-methylpropyl)(1-methylpropyl)]ketne (13).

INTRODUCTION

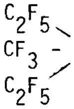
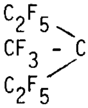
As part of our study [2] of the reactions of tetrafluoroethene oligomers, we have recently reported [1] the preparation of a number of epoxides obtained by the direct reaction of the corresponding perfluoroalkenes with sodium hypochlorite. The most widely reported perfluorooxiran, hexafluoropropene oxide (HFPO), has been extensively used as a source of difluorocarbene by thermal decomposition [3], its chemistry and that of related compounds have been reviewed [4]. A disadvantage of (HFPO) is its fairly low boiling point (-27°) so that it is not easy to store and handle. In contrast the oxirans from TFE pentamer (1) and hexamer (2) are high boiling, easily handleable liquids and in principle might be good sources of CF_3CF: and CF_2: respectively.

This is supported by consideration of models of the two compounds, both the pentamer and hexamer derivatives would be expected to have considerable steric crowding due to the bulky perfluoroalkyl groups, whereas the products from loss of CF_3CF: and CF_2:, respectively, the ketones  and  should be much less strained.

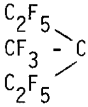
RESULTS

We have examined the thermal stabilities of the oxirans (1) and (2) over a wide range of temperatures using a flow pyrolysis method with pyrex glass pieces as column packing similar to that described previously in our study of the thermolysis reactions of the oligomers themselves and their fluorinated derivatives [5].

Firstly the oxirans were pyrolysed alone, and then in the presence of bromine and toluene as radical sources, and cyclohexene as a carbene trap.

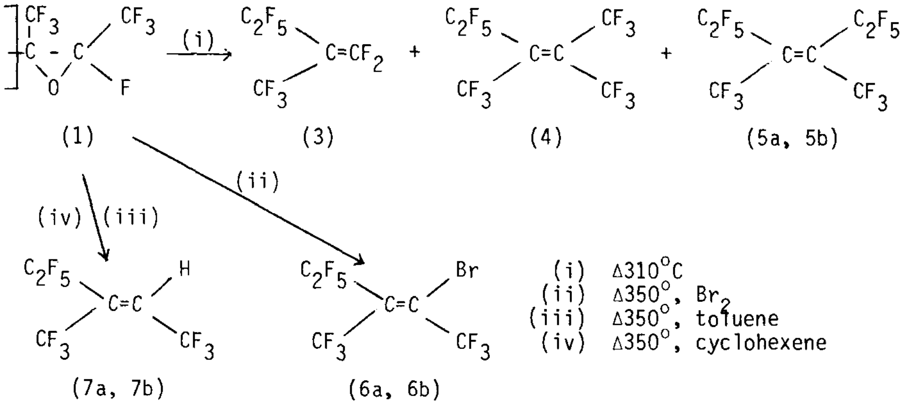
Oxiran (1) was significantly more stable to heat than is HFPO, the latter decomposes at 180-200°C, but (1) only decomposed significantly on pyrolysis near to 300°. At this temperature (1) afforded a reasonable yield of a mixture containing three major products and five very minor components. Separation of the mixture by gas chromatography afforded the three major components in almost equal amounts. They were easily identified (by a comparison of the i.r. and ^{19}F n.m.r. spectra with those of authentic samples) as perfluoro-2-methylbut-1-ene (3), perfluoro-2,3-dimethylpent-2-ene (4) and (E) and (Z) perfluoro-2,3-dimethylhex-3-ene (TFE tetramer) (5a, 5b) (see Scheme 1). No products attributable to the elimination of trifluoromethylcarbene were identified, but trifluoroethanoylfluoride was present (i.r. spectrum). Previously [6] we have shown that co-pyrolysis of fluorocarbons (including oligomers of TFE and their fluorine adducts [5]) with bromine or toluene distinguishes the pathways of thermal decomposition, bromine or hydrogen appearing in the products at positions corresponding with the rupture of the weakest bond. Oxiran (1) was pyrolysed with bromine at 300-350°. Only one product was formed in good yield. This was identified by ^{19}F n.m.r., elemental analysis and mass spectrometry. The latter showed the presence of one bromine atom, indicated by the molecular ion as the characteristic doublet at 260 and 262 mass units, corresponding to an empirical formula of C_6BrF_{11}. The ^{19}F n.m.r. spectrum confirmed the disappearance of the  $CF_3-C(C_2F_5)_2$-group and showed two groups of peaks in the ratio 55/45. These data are consistent with the compound being (E) and (Z)-2-bromoperfluoro-3-methylpent-2-ene (6a, 6b). Co-pyrolysis of oxiran (1) with toluene afforded a mixture of two major components in equal proportions. ^{19}F and ^{1}H n.m.r. spectroscopy indicated the product was a mixture of closely related compounds probably E and Z isomers. The ^{19}F spectrum again showed the loss of the characteristic  $CF_3-C(C_2F_5)_2$-group and indicated the presence of three trifluoromethyl groups, two of which were attached to a double bond, there was also a single CF_2 group. The ^{1}H spectrum showed a single resonance, a quartet with further small coupling. Elemental analysis corresponded to a formula of C_6HF_{11}. These data suggest the product to be a mixture of the E and Z isomers of 2H-perfluoro-3-methylpent-2-ene (7a, 7b). It was found possible to separate the isomers on semi-preparative g.l.c. The ^{19}F spectra of the individual isomers were measured and, on the basis of the chemical shift differences, it was possible to assign structures for each isomer.

A similar result was obtained when oxiran (1) was co-pyrolysed with cyclohexene, compounds (7a, 7b) being the only isolable products. Nothing corresponding to the direct trapping of the carbene intermediate was detected.

The postulation of release of strain as outlined above suggested that oxiran (2) should be a good precursor of difluorocarbene. Accordingly compound (2) was heated with cyclohexene under a variety of conditions (see Scheme 2). No decomposition seemed to occur below 175° but at this temperature and above, the oxiran readily decomposed. However, no products attributable to difluorocarbene formation could be detected. It is known from previous work [3] with HFPO and cyclohexene that the carbene adduct, difluoronorcarane, is stable at 180° and to test our methodology we repeated this experiment and obtained similar results. Thus, we conclude that difluorocarbene extrusion is not a significant decomposition pathway for oxiran (2). When the latter and cyclohexene were heated together in a sealed tube at 175° for 24 hr, three products resulted, which were separated by g.l.c. The first product isolated was a liquid with strong bands in its i.r. spectrum at 1860 cm^{-1} indicative of the presence of an acid fluoride and at 1620 cm^{-1} suggesting a C=C bond. ^{19}F n.m.r. spectroscopy again indicated the absence of the  $CF_3-C(C_2F_5)_2$-group; chemical shifts and the integration pattern suggested the presence of one tertiary fluorine atom, two CF_3 groups and two CF_2 groups contained in a mixture of E and Z isomers. Mass spectrometry indicated, from the highest mass peak and the breakdown pattern, an empirical formula of $C_{10}F_{18}O$, which corresponds to perfluoro-3-methyl-2-(1-methylpropyl)-pent-2-en-1-oylfluoride (11). The second component was readily identified as pentafluoroethylcyclohexane (12) and the third component as 'hexamer' ketene (13).

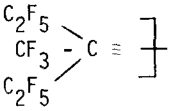
When oxiran (2) was pyrolysed in the flow system at 330° a single non-gaseous compound, readily identified as perfluoro-2-methylbut-1-ene (3), was formed; no other major product could be detected. Pyrolysis of the oxiran (2) in the presence of bromine gave two products in fairly good yield, in approximately equal amounts. Separation by preparative g.l.c. afforded the known 3-bromoperfluoro-3-methylpentane (9) and a previously unknown compound which showed peaks in its mass spectrum at m/e 357 and 359 and at m/e 297 corresponding to $C_6BrF_{10}O$ and $C_6F_{11}O$ respectively. Other peaks at m/e 247 $(M-CF_2Br)^+$ and m/e 129 and 131 $(CF_2Br)^+$ were useful in structural determination. The i.r. spectrum showed a strong band at 1780 cm^{-1} (C=O) and the ^{19}F n.m.r. spectrum showed C_2F_5, CF_3 and CF_2Br and a tertiary fluorine atom. These data suggest the product to be 1-bromo-3-trifluoromethylheptafluoropentan-2-one (8). Reaction of (8) with dimethylamine afforded N,N-dimethylbromodifluoroethanamide, via a haloform cleavage, thus supporting the structure (8).

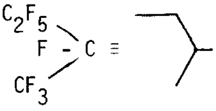
Thermolysis of oxiran (2) in the presence of toluene afforded (3) and 3H-perfluoro-3-methylpentane (10) and no significant oxygen containing products.



Scheme 1

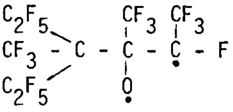
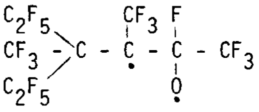
In all schemes:

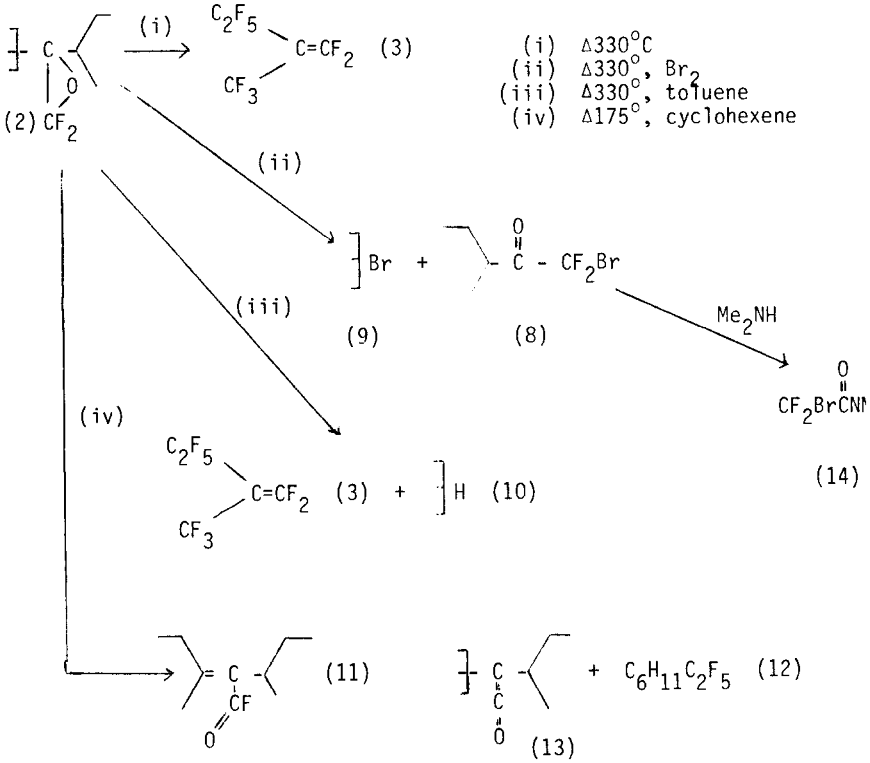




DISCUSSION

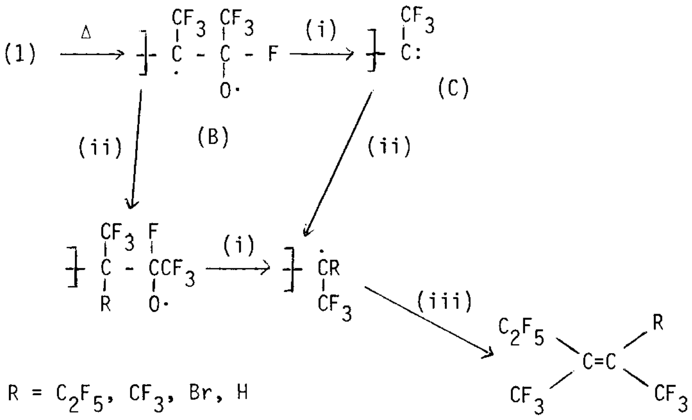
From these results it is clear that there is little, if any, formation of the carbenes $:CF_2$ or $:CFCF_3$ in these pyrolytic reactions. The decompositions seem to be controlled by the relative stabilities of the radicals formed by rupture of the weakest bonds, but the further decomposition of these radicals do not give these particular carbenes. If we consider first the oxiran (1), assuming C-O bond cleavages as the first step, and most of the products of decomposition would appear to be in conformity with this, then the two diradicals which can form:


(A) and

(B)



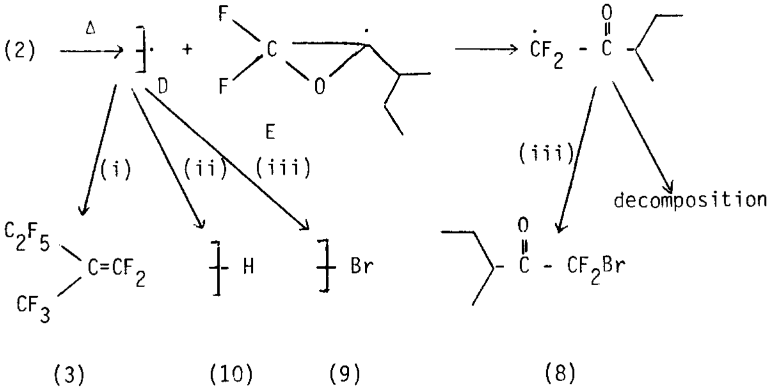
(i) Δ330°C
(ii) Δ330°, Br_2
(iii) Δ330°, toluene
(iv) Δ175°, cyclohexene

Scheme 2



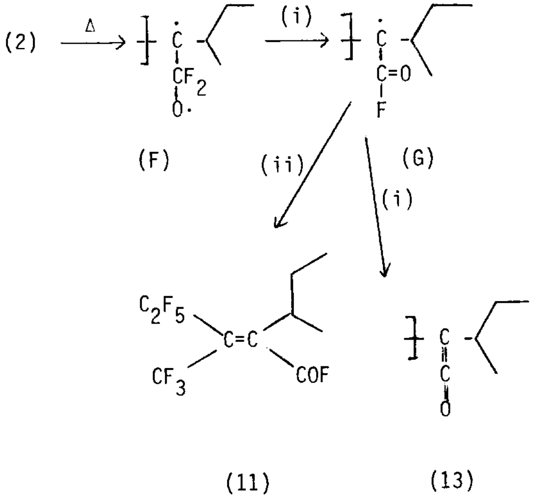
R = C_2F_5, CF_3, Br, H
(i) loss of CF_3COF
(ii) addition of R·
(iii) loss of C_2F_5

Scheme 3



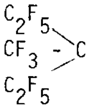
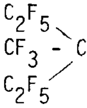
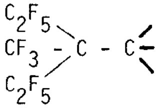
(i) loss of CF_3
(ii) toluene
(iii) Br_2

Scheme 4



(i) loss of F·
(ii) loss of $C_2F_5^{\cdot}$

Scheme 5

From our previous work [5,6] showing that the most heavily substituted radicals are favoured, a conclusion also supported by others [7], diradical (B) seems the more likely. B now has two possible modes of reaction as outlined in Scheme 3, though additions to it seem less likely than loss of CF_3COF to give carbene C. Additions to carbene C by species present account for most of the products found. The exception is perfluoro-2-methylbut-1-ene (3). This product has appeared previously [5] in the pyrolysis of a product containing the  $CF_3-C(C_2F_5)_2-$ group, and clearly comes from the radical  $CF_3-\dot{C}(C_2F_5)_2$ (D) by loss of CF_3. The cleavage of the central bond in a species of type  $CF_3-C(C_2F_5)_2-C\lessdot$ is a facile process [5]. In the present case, cleavage in the oxiran (1) of this type of bond to give two radicals competes to some extent with C-O cleavage of the oxiran ring. Alternately, the radical (D) could arise from breakdown of diradical (B).

Rupture of bonds of this type must occur in the thermal decomposition at higher temperatures of oxiran (2), either alone, or in the presence of toluene, when the isolated products can all be accounted for in terms of a cleavage to give the same radical (D) which can respectively give (3) and (10) (Scheme 4). This is in keeping with previous results [5] and parallels some of our recent work [9] with perfluoro[(1-ethyl-1-methylpropyl)(1-methylpropyl)]ethanolide [8]. The fact that only products (3) and (10) were isolated suggests deep seated breakdown of the other radical formed (E) to give small fragments. In fact, only the pyrolysis in the presence of bromine confirms the reality of this decomposition pathway. Here, the more ready extraction/formation of bromine radicals allowed the direct trapping of both intermediates D and E leading to the isolation of bromo-compounds (8) and (9). At lower temperatures (175-180°) in the presence of cyclohexene, oxiran (1) was recovered unchanged in virtually quantitative amounts. However, in a static reaction with cyclohexene, oxiran (2) gave three products ((11), (12), (13) Scheme 2) and (11) and (13) clearly arise from a different pathway. Compound (12), the minor product, presumably arises from reaction of C_6H_{10} with some $C_2F_5\cdot$ formed in the breakdown of the molecule as above. However, it is suggested that (11) and (13) require the involvement of the alternative breakdown of (2), i.e. C-O bond cleavage of the oxiran ring as shown in Scheme 5 to give diradical F. This breakdown pattern could have given rise to difluorocarbene. However, the other C-O bond breaks to give diradical F followed by loss of F· to give the acyl fluoride radical G. There then occurs either loss of $C_2F_5\cdot$ to form the acid fluoride (11) or rather more surprisingly loss of the "acyl" fluorine and the formation of the ketene (13). This again demonstrates the high thermal stability of bisperfluoroalkylketenes.

Although these thermal decompositions did not give the desired route to simple fluorocarbenes, they have nonetheless proved interesting. Oxiran (1) has a relatively high thermal stability in keeping with its high chemical inertness [1]. This stability is markedly lowered with increased steric crowding at one of the carbons in oxiran (2) in keeping with earlier results on the thermal stability of fluorocarbon derivatives.

EXPERIMENTAL

Apparatus The pyrolysis tube was constructed of pyrex glass (75 cm x 1.5 cm) packed with small pieces of pyrex glass tube (*ca.* 1 cm long x 0.4 mm) mounted vertically and heated by means of electric fire elements wound in channels in fire bricks for 50 cm of its length. Gas chromatography was carried out using a Pye 104 series machine with a semi-preparative attachment using the columns specified.

Pyrolysis of perfluoro-2,3-dimethyl-2-(1'-ethyl-1'-methylpropyl) oxiran (pentamer epoxide) (1) The oxiran (112.5 g) was introduced into the pyrolysis tube at 305-310°C over 5.5 hr in a stream of dry nitrogen ($5\ dm^3\ h^{-1}$), the products being collected in a glass trap cooled in liquid air. The contents of the trap were slowly warmed via a trap cooled in solid carbon dioxide then ice salt (-15°) to room temperature. Examination of the volatile materials by i.r. spectroscopy showed the presence of silicontetrafluoride and trifluoroethanoylfluoride. The residue (57.4 g) was examined by analytical gas chromatography and was shown to contain three major and five very minor components. Gas chromatographic separation of a sample (2.5 g) of the mixture (Diisodecylphthalate Chromasorb P (1:3, 45°, N_2, $1\ dm^3\ h^{-1}$) gave (i) a mixture of four very volatile components (0.3 g) not identified; (ii) perfluoro-2-methylbut-1-ene (3) (0.42 g) identified by comparison of i.r. and ^{19}F n.m.r. spectra with those of an authentic sample [5]; (iii) perfluoro-2,3-dimethylpent-2-ene (4) (0.5 g), b.p. 71-72° identified by comparison of i.r. and ^{19}F n.m.r. spectra [2] and by mass spectrometry (m/e 331 (M-F), m/e 281 ($M-CF_3$), 231 ($M-C_2F_5$). C_7F_{14} requires

M 350); (iv) E and Z perfluoro-2,3-dimethylhexene (TFE tetramer) (5a and b) (0.6 g) identified by comparison with an authentic sample.

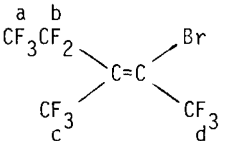
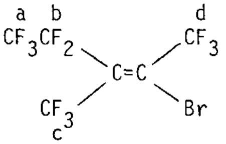
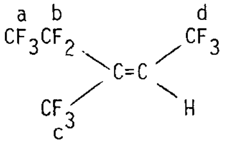
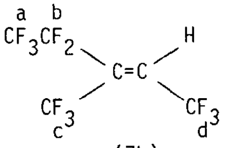
Co-pyrolysis of (1) with bromine The oxiran (25.8 g) and bromine (87 g, 28 cm^3) were simultaneously added to the pyrolysis tube at 350°C in a stream of nitrogen (2 dm^3 h^{-1}) over a period of 5 hr. The products were collected in a glass trap cooled in liquid air. Any volatile material (less than 1 g) was allowed to evaporate off and the residue was treated at 0-10° with precooled sodium metabisulphite solution. When all the excess bromine had been removed the fluorocarbon layer was separated and washed with water (100 cm^3). The residue (14.9 g) was dried (P_2O_5) and distilled in vacuo by trap to trap transfer. Analytical gas chromatography revealed the presence of one major (>90%) component with traces of minor products. Purification of a sample (1 g) by semi-preparative g.l.c. (Peg A/Chromasorb P 1:6, 80°, N_2, 1.5 dm^3 h^{-1}) gave E and Z 2-bromo-undecafluoro-3-methylpent-2-ene (6a and b) nc (.71 g), b.p. 94°C (Found: C, 19.9; Br, 22.1; F, 58.2% M (mas spec.) 260/262. C_6BrF_{11} requires C, 19.9; Br, 22.1; F, 57.9% M 260/262). The ^{19}F n.m.r. spectrum showed two groups of peaks in the ratio 55:45 attributable to the E and Z isomers distinguishable by the CF_3-CF_3 couplings (see Table).

Co-pyrolysis of (1) with toluene The epoxide (25.8 g) and toluene (110 g) were co-pyrolysed at 350°C in a stream of nitrogen (2 dm^3 h^{-1}) over 6 hr. The product (10.7 g), after separation from the toluene (the large excess of toluene was shown by g.l.c. to contain about 15% (ca. 5-6 g) of components with the same g.l.c. retention time and ^{19}F n.m.r. spectrum as those in the fluorocarbon layer and no attempt was made to separate them) was shown by analytical g.l.c. to contain two components in equal proportions. Separation of a portion (1.12 g) by semi-preparative g.l.c. (Dinosylphate/Chromasorb P 1.10, 55°, N_2, 1.8 dm^3 h^{-1}) gave (i) Z-2H-perfluoro-3-methylpent-2-ene (7a) nc (0.36 g), b.p. 42°C (Found m/e 263 (M-F), m/e 213 (M-CF_3), m/e 163 (M-C_2F_5). $C_6F_{11}H$ requires M 282; (ii) E-2H-perfluoro-3-methylpent-2-ene (7b) nc (0.34 g), b.p. 52°C (Found m/e 263 (M-F $C_6F_{11}H$ requires M 282). Elemental analysis on a mixture of (7a) and (7b) gave: C, 25.8; H, 0.5. C_6HF_{11} requires C, 25.5; H, 0.3%.

Co-pyrolysis of (1) with cyclohexene In a similar experiment to the above the oxiran (25.8 g) and cyclohexene (63 g) gave (7a) and (7b) (15.9 g) in the same proportions.

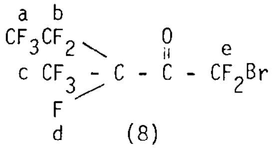
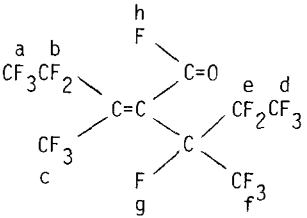
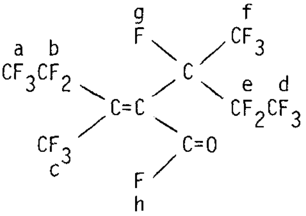
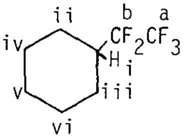
TABLE

NMR DATA

Compound		Chemical Shift	Rel. Int.	Assign- ment	Coupling
 (6a)	^{19}F				
		-56.1	3	c	c
		-59.3/60.1	3	d	c
		-80	3	a	q J_{ac} 8 Hz
		-107.5	2	b	q J_{bc} 22 Hz
 (6b)	^{19}F				
		-58.4	3	c	qt J_{bc} 23 Hz
		-59.3/60.1	3	d	c
		-79.9	3	a	st $J_{ac} = J_{ad} =$ 8 Hz
		-103.0	2	b	qq J_{bd} 20 Hz
 (7a)	^{1}H	6.35			cq J_{Hd} = 7.5 Hz
	^{19}F				
		-59.2	3	c	c
		-63.8	3	d	c
		-82.9	3	a	c
		-110.8	2	b	c
 (7b)	^{1}H	6.25			cq J_{Hd} 7.5 Hz
	^{19}F				
		-62.3	3	c	e
		-62.7	3	d	c
		-87.1	3	a	q J_{ac} = 6 Hz
		-116.1	2	b	q J_{bc} = 10 Hz

(Continued overleaf)

TABLE (Cont.)

Compound		Chemical Shift	Rel. Int.	Assign-ment	Coupling
 (8)	^{19}F	-64.1	2	e	s
		-74.1	3	c	c
		-83.3	3	a	c
		-121.5	2	b	cAB J_{AB} 300 Hz $\Delta\nu_{AB}$ = 180 Hz
		-189.4	1	d	c
 (11a)	^{19}F	+57.3	1	h	c
		-52.9	3	c	cd J = 60 Hz
		-69.3	3	f	c
		-79.3	3	a	c
		-79.6	3	d	c
		-103.1	2	b	c
		-115.9	2	e	cAB
		-174.2	1	g	c
 (11b)	^{19}F	+56.4	1	h	c
		-57.4	3	c	c
		-68.9	3	f	c
		-77.7	3	a	c
		-78.1	3	d	c
		-103.1	2	b	c
		-115.5	2	e	cAB
		-172.4	1	g	c
	^{1}H	1.27	5	i ii iii	c
		1.88	6	iv v vi	c
	^{19}F	-82.5	3	a	s
		-122.3	2	b	$^{d}J_{bi}$ 145 Hz

Pyrolysis of perfluoro-2-(1-ethyl-1-methylpropyl)-2-(1-methylpropyl) oxiran (2) The oxiran (10 g) was pyrolysed in a stream of nitrogen (3 dm^3 h^{-1}) at 330° over 3 hr. The products (7.9 g) were trapped in a glass trap cooled in liquid air. The volatile components (mainly SiF_4 and CF_3COF) were allowed to evaporate and analytical gas chromatography showed the residue to be mainly one component. Purification by semi-preparative g.l.c. afforded perfluoro-2-methylbut-1-ene (3) identical with an authentic specimen.

Co-pyrolysis of (2) with bromine The oxiran (14 g) and bromine (37 g, 12 cm^3) were co-pyrolysed at 330° in a stream of nitrogen (2 dm^3 h^{-1}). The product was washed successively with 25% sodium metabisulphite solution and water to give a fluorocarbon layer (11.43 g). Separation of a sample (0.63 g) by semi-preparative gas chromatography afforded (i) 1-bromoperfluoro-3-methylpentan-2-one (8) nc (0.27 g), b.p. 89°C (Found: C, 18.9; F, 55.4; Br, 21.4%. $CBrF_{11}O$ requires C, 19.1; F, 55.4; Br, 21.2%); (ii) 3-bromoperfluoro-3-methylpentane (9) (0.25 g) identical to an authentic sample [5].

Co-pyrolysis of (2) with toluene The oxiran (12.3 g) was co-pyrolysed with toluene (92 g) at 330-340° in a stream of nitrogen (2 dm^3 h^{-1}). The product (7.8 g) was shown by analytical gas chromatography to consist of mainly two components. Separation of a portion (1.25 g) afforded (i) perfluoro-2-methylbut-1-ene (3) (0.25 g) and (ii) 3H-perfluoro-3-methylpentane (10) (0.32 g) both identical to authentic samples [5].

Co-pyrolysis of (2) with cyclohexene The oxiran (2) (24.6 g) and cyclohexene (4.0 g) were heated together in a sealed Carius tube at 175°C for 24 hr. The products (20.2 g) were distilled *in vacuo* to give a clear liquid (17.2 g) and a polymeric solid (3 g). A portion (4.24 g) of the liquid was separated by semi-preparative gas chromatography to give (i) perfluoro-3-methyl-2-(1-methylpropyl)-pent-2-enoyl fluoride (11a and 11b) nc (1.7 g), b.p. 116°C (Found: C, 24.8; F, 71.8%. $C_{10}F_{18}O$ requires C, 25.1; F, 71.5%). ^{19}F n.m.r. spectroscopy indicated a mixture of E and Z isomers; (ii) pentafluoroethylcyclohexane (12) nc (0.3 g), b.p. 114°C (Found: C, 47.0; H, 4.8; F, 47.0%. $C_8H_{11}F_5$ requires C, 47.6; H, 5.4; F, 47.0%); (iii) perfluoro-3-(3-methylpentyl)-2-(2-butyl)ketene (hexamer-ketene) (13) (1.1 g) [12]; (iv) unreacted starting material (0.3 g).

Reaction of 1-bromoperfluoro-3-methylpentan-2-one with dimethylamine

The ketone (5.7 g) was added over 15 min to a solution of dimethylamine in dry ether (30 cm^3) at -10°C. The mixture was stirred and allowed to warm to 15° over 15 min. After filtration to remove a small amount of an unidentified white solid, the ether was removed by vacuum transfer. The residue (3.4 g) was distilled *in vacuo* to yield N,N-dimethylbromodifluoroethanamide (14) nc (1.38 g), b.p. 176°C (Found: C, 23.9; H, 2.8; Br, 40.1; F, 18.3; N, 7.2%. $C_4H_6BrF_2NO$ requires C, 23.8; H, 3.0; Br, 39.6; F, 18.8; N, 6.9%). Mass spectrometry gave a molecular ion peak at m/e 201/203 in the correct ratio for one bromine atom being present.

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