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REACTIONS OF TETRAFLUOROETHENE OLIGOMERS PART 11 [1] FLASH VACUUM THERMOLYSIS OF SOME PRODUCTS DERIVED FROM THE PENTAMER AND HEXAMER OLIGOMERS.

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SUMMARY

Flash vacuum thermolysis of a variety of derivatives of tetrafluoroethene oligomers in the temperature range 450–600° at 20mm – 0.4mm Hg affords a number of unusual products. Thus, the pentamer (1) affords perfluoro 1,2,3- trimethyl cyclobutene (2), E and Z perfluoro-2,3-dimethylpentadiene (3,) (4) as previously reported, but in much different ratios. The diazoalkane (5) affords E and Z-3H-perfluoro-4-methylhex-3-ene (6) (7) and the diene E/Z - 4H,5H - perfluoro-3,6-dimethyl octa-3,5-diene (8):perfluoro (2,3-dimethyl-3 (3-methylpentyl)) azirine (9) gives E/Z-2-cyano -perfluoro-3-methylpent-2-ene (10,11). Perfluoro-(2,3-dimethyl-2-(3-methylpentyl)) oxiran (12) gives a mixture of perfluoro-2-methylbut-1-ene (13) and perfluoro-2, 3-dimethylpent-2-ene (14). The hexamer oligomer of TFE (15) affords perfluoro-1 -methyl-2-(1-methylpropyl) cyclobut-1-ene (16) and E/Z perfluoro-2 -methyl-3-(1-methylpropyl)buta-1,3-diene (17) identical to previous results but again in significantly changed ratio. The corresponding oxiran (18) yielded only the butene (13). Perfluoro-4-ethyl-2,3,4,5-tetra methyl-2,3-epoxy-4,5-dihydrofuran (19) gave a mixture of perfluoro-3-methylpent-2-ene (TFE trimer)(20) and perfluorobiacetyl (21). Only at low temperatures was any of the α,β unsaturated ketone (22) isolated in small yield. This latter is the main product from conventional thermolysis. 4H-perfluoro-3, 5-dimethyl-5-ethylhept-3-ene (23) gave an E/Z mixture of the novel diene 3H-perfluoro-2,4-dimethylhexa-1,3-diene (24) (25). Perfluoro-3,5-dimethyl-3-ethylheptanone (26) or the ethanolide derived from ketene (29) afforded a mixture of the butene (13) and perfluoro-2-methylbutane (27). Perfluoro (1-ethyl-1(methylpropyl) (1-methylpropyl))keten (29) gave a mixture of perfluoro-4-methylhexyne (30), perfluoro-5-methylheptyne (31) and the unusual perfluoro-1-(1-methylpropyl) -2-methylcyclopropene (32).

Thus, we have produced a wide range of very interesting compounds using a very simple technique. The mechanisms of the production of these species are discussed.

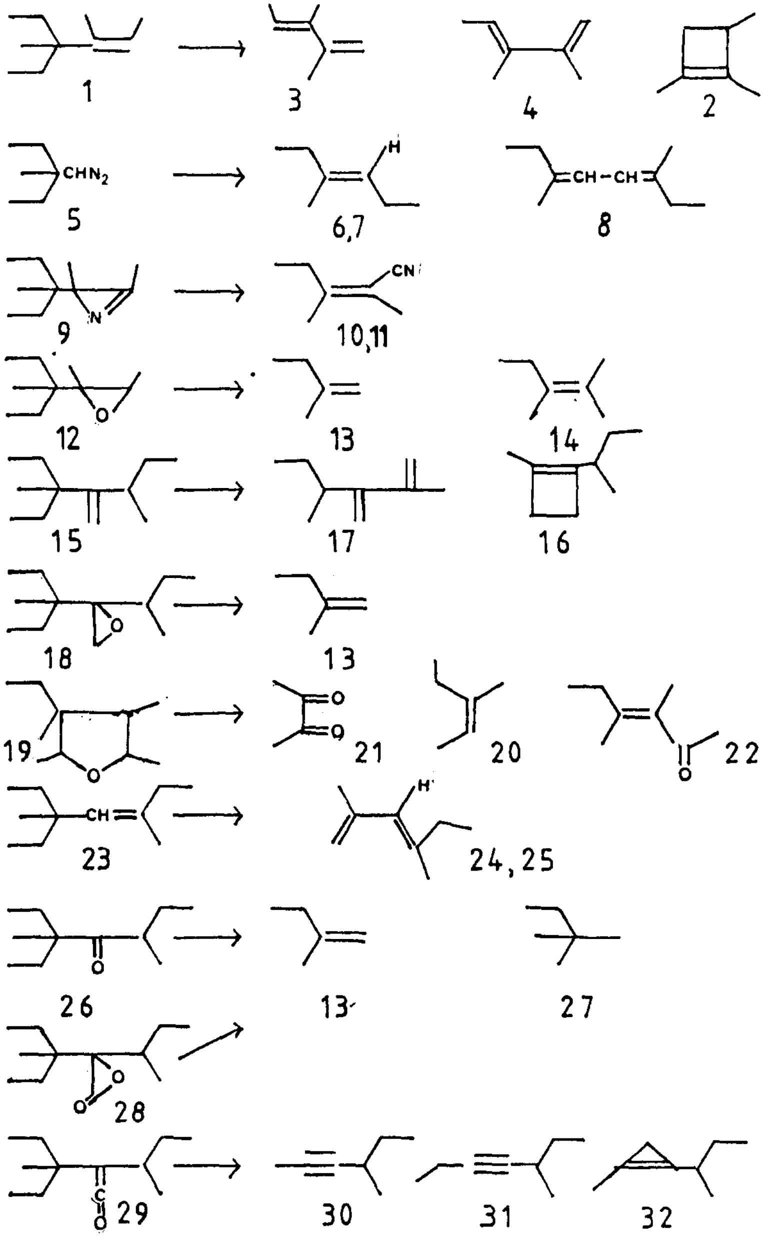
INTRODUCTION

Thermolysis of fluorocarbons to produce unusual species is well known and has been exhaustively reviewed [2]. Frequently thermolysis has taken place at atmospheric pressure and we have reported previously some studies of the thermolysis of TFE oligomers and some derivatives at ambient pressures [3] [4]. Recently, flash vacuum thermolysis (FVT) has become a popular technique with claims that, due to the short contact times, higher temperatures may be used and that reactive species are formed and leave the hot zone very quickly to give, by various quenching procedures, unusual products. This area has recently been reviewed [5]. We therefore decided to investigate the use of (FVT) on some derivatives of the pentamer and hexamer oligomers of tetrafluoroethene.

DISCUSSION

In the light of our previous work [3] [4] we decided first to study the thermolysis of the pentamer oligomer(1). Reaction at 500°/15mm gave a mixture of three products which were readily separated and identified as the cyclobutene (2) and the dienes (3) and (4) (Scheme 1). These were identical to the products formed by conventional pyrolysis [3] however in this case the ratio of the products was 1:4:5 but in the present study the ratio was 1:3:3.5 i.e. significantly more cyclobutene was obtained. Thus, it would appear that FVT does disturb the equilibrium between the diene and the cyclobutene, since in the conventional pyrolysis reaction the contact time in the heated zone is much greater.

We next reacted the diazoalkane (5) under similar conditions. Three components were isolated in good yield. It was clear from preliminary ^{19}F and ^{1}H n.m.r. studies that two components were E and Z isomers by the similarity of their spectra. The ^{19}F spectrum showed in each case bands for two C_2F_5 groups and a CF_3 group and the ^{1}H n.m.r. spectrum gave a triplet signal for an olefinic proton. These data and the mass spectrum show the products to be E and Z - 3H-perfluoro-4-methylhex-3-ene (6) (7). Tentative assignment of the E and Z isomers is by the slightly different chemical shifts of the $-CF_2-$ in one of C_2F_5 groups and by the use of chemical shift parameters of the H shift. The third component was shown also by ^{19}F and ^{1}H n.m.r. spectroscopy to be an inseparable mixture of E and Z isomers. The ^{19}F spectrum indicated the presence of C_2F_5 and CF_3 groups and the proton spectrum olefinic hydrogens. The mass spectrum and elemental analysis indicated these products to be $C_{10}H_2F_{16}$ and these data taken together are consistent with the structure being E/Z 4H/5H-perfluoro-3,6-dimethylocta-3,5-diene (8).



All unmarked bonds joined to fluorine

Scheme 1

We next pyrolysed the aziridine (9) [6] and again on the basis of ^{19}F n.m.r. spectroscopy obtained a 3:2 mixture of E and Z isomers. The i.r. spectrum of the product showed a strong band at 2240 cm^{-1} indicative of a nitrile. The ^{19}F n.m.r. spectrum was similar to that for compounds (6,7) showing a C_2F_5 group and two CF_3 groups. Elemental analysis and mass spectrometry confirmed the structure as E/Z 2-cyano-perfluoro-3-methylpent-2-ene (10) (11).

Thermolysis of the pentamer and hexamer epoxides (12) (18) gave the same products as previously described [3] for the atmospheric pressure thermolysis namely perfluoro-2-methylbut-1-ene (13) and perfluoro-2,3-dimethylpent-2-ene (14).

However reaction of the hexamer (15) was somewhat different to the earlier pyrolysis and showed a considerable temperature dependence. The early work [3] showed that the major product, the cyclobutene (16) was obtained in an 18 : 1 ratio over the minor product the diene (17). In the present study, we found that at 450° the ratio was close to 1 : 1 whereas at 590° the ratio was 7 : 3 i.e. higher temperatures favour cyclisation, in keeping with the well known thermal cyclodimerisation of tetrafluoroethene and its derivatives.

Reaction of the epoxyether (19) also showed a significant difference to the results obtained earlier [7]. In this study the major product from the thermolysis was the α,β unsaturated ketone (22) and more recent work [8] has shown it is possible to obtain (22) as 90% of the product mix. The other product isolated was the trimer of TFE (20). In the present work a pale yellow liquid was isolated which depending on the temperature used was a two component (550°/0.4mm) or three component mixture (440°/0.4mm). Separation of the mixture from the 550° run yielded a low boiling yellow liquid readily identified by its ir and ^{19}F n.m.r. spectrum as perfluorobiacetyl (21) previously prepared by a longer route [9]. The second component was shown to be TFE trimer (20).

Separation of the product mixture from the higher temperature run gave (20) (21) and (22) in the ratio 22 : 10 : 1 in strong contrast to the previous results.

The thermolysis of the olefin (23) afforded a mixture of two components which could be separated. The i.r. spectra showed strong diene absorptions at 1745 cm^{-1} and 1740 cm^{-1} respectively. The mass spectra and elemental analysis of each component indicated the products to be the C_8HF_{13}. The ^{19}F n.m.r. spectrum of both components showed the presence of two CF_3 groups a C_2F_5 group and a $=CF_2$ group. The pattern of peaks for the $=CF_2$ and the CF_3 group at 63.5, 72.8 and 74.5 ppm is similar to that found previously [3] for $CF_2 = CCF_3R$ in several compounds. e.g. $CF_2{=}CCF_3C_2F_5$ and $CF_2{=}CCF_3{-}CCF_3{=}CFCF_3$. The ^1H spectrum showed complex peaks at 6.40δ and 6.73δ respectively. On the basis of chemical shift parameters of fluoroalkyl and alkenyl groups we can assign the compound with the ^1H signal at 6.40δ

as having the Z configuration at its $-CH{=}C\ CF_2CF_3$ double bond and the other isomer with the E configuration. Thus the two products are the dienes (24) and (25).

Reaction of the ketone (26) and the ethanolide (28) proved to be uninteresting both forming the olefin (13) and the methyl butane (27).

Finally, thermolysis of hexamer ketene (29) gave a mixture of three products in the ratio 6 : 2 : 1. Separation of the mixture gave first a volatile liquid, the major component. The i.r. spectrum gave a strong band at 2010 cm^{-1} characteristic of an alkyne. The ^{19}F n.m.r. spectrum showed the expected pattern for the perfluoro 2-butyl group and one other signal for a CF_3 group at −65.2 ppm which we assign to a CF_3 group bonded to a triple bond. The mass spectrum gave a molecular ion peak at m 312. It was not possible to obtain an elemental analysis due to the volatility of the material. Thus, we assign the structure as perfluoro-4-methylhex-2-yne (30).

The second component similarly was a volatile liquid and again showed a strong band at 2010 cm^{-1} in the i.r. spectrum and the ^{19}F n.m.r. spectrum showed the perfluoro-2-butyl group and a C_2F_5 group. The mass spectrum gave a m of 362 the molecular ion for the product being perfluoro-5-methylhept-3-yne (31).

The third component showed a double band absorption at 1750cm^{-1}. The ^{19}F n.m.r. spectrum again showed the presence of a perfluoro-2-butyl group, a CF_3 group and a difluoromethylene group which was prochiral having an AB system (J_{AB}282Hz Δ_{AB}316Hz). These data agree closely to those for perfluorocyclopropenes previously described [10] [11] and we assign the structure of the product as perfluoro -1-(1-methylpropyl)-2-methylcyclopropene (32). These results are summarised in Scheme 1. Thus, the thermolyses we have described have produced a remarkable series of new compounds from readily available materials.

A first sight there does not to be a simple rationale for the formation of the wide range of products formed in these reactions, but closer examination shows that for all of the compounds containing the $(C_2F_5)_2CF_3C$ group, with the exception of the diazoalkane (5) and the oxirans (12) and (18), the ketone (26) and the ethanolide (28) there is a common step, the loss of a C_2F_5 group to give the corresponding alkyl radical as was previously proposed [3], and even in the case of oxiran (12) one of the products can be attributed to this pathway. The subsequent steps depend very much on the nature of the remainder of the molecule as is shown in Scheme 2.

The diazoalkane (5) appears to break down by a different route. Not unexpectedly it seems that a likely pathway is loss of nitrogen to form the carbene (33) which may then rearrange by migration of a C_2F_5 group to the isolated products (6,7). A similar pathway has been proposed previously for the photochemical decomposition of heptafluorodiazobutane [12] when a major product is 2H-perfluorobut-1-ene. Dimerisation of the carbene to give the intermediate (34) is a second likely possibility and again the ready loss of a C_2F_5 group to give the allyl radical (35) which can further lose C_2F_5 to give the observed diene (8) (see Scheme 2).

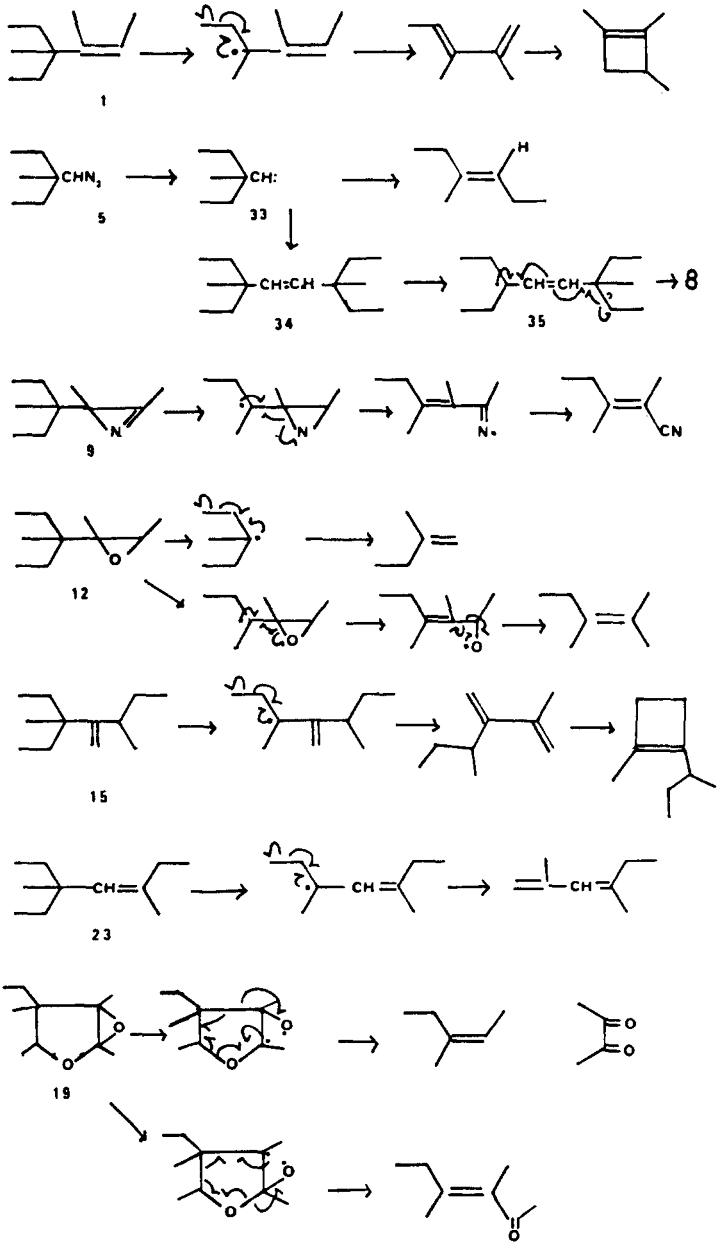
The oxirans (12) and (18) the ketone (26) and the ethanolide (28) all decompose by a different route as shown in Scheme 3. In these cases loss of the $(C_2F_5)_2CF_3C$ group seems to be preferred and the radical derived from this leads to the major product, the alkene (13). We would have expected the ethanolide (28) and ketone (26) to give the same product since we know the conversion of (28) to (26) proceeds to completion at ca 80° very rapidly. It should be noted however that the minor product for the reaction of (12) can readily be explained by loss of C_2F_5 as above.

The formation of the alkynes (30) and (31) and the cyclopropene (32) from the ketene (29) is worthy of discussion. As indicated in Scheme 4 we propose the loss of C_2F_5 to give the intermediate olefin and on the basis of previous evidence we would expect this to cyclise cf $1\rightarrow2$ and $15\rightarrow16$. However, the product in this case, the cyclobutenone has two possible modes of decomposition, retrocyclo-addition to give the observed alkyne (30) and decarbonylation to give the cyclopropene (32). There is a good deal of evidence from our own work [13] and that reported in the review by Platanov and Yakobson [2] that decarbonylation of cyclic fluoroketones is a facile process. An alternative route could be the in situ formation of difluorocarbene followed by its addition to the alkyne (30) in the manner described by Mahler [11] for the formation of perfluoro 1,2-dimethyl cyclopropene from hexafluorobut-2-yne. If this were the case we might have expected to see some of the bicyclobutane (36) from addition of a second carbene or its rearrangement product the cyclobutene (37). We see neither of these products and favour the decarbonylation route. The alkyne (31) we suggest might arise from a rearrangement of (32) as indicated or from the decarbonylation step directly.

EXPERIMENTAL

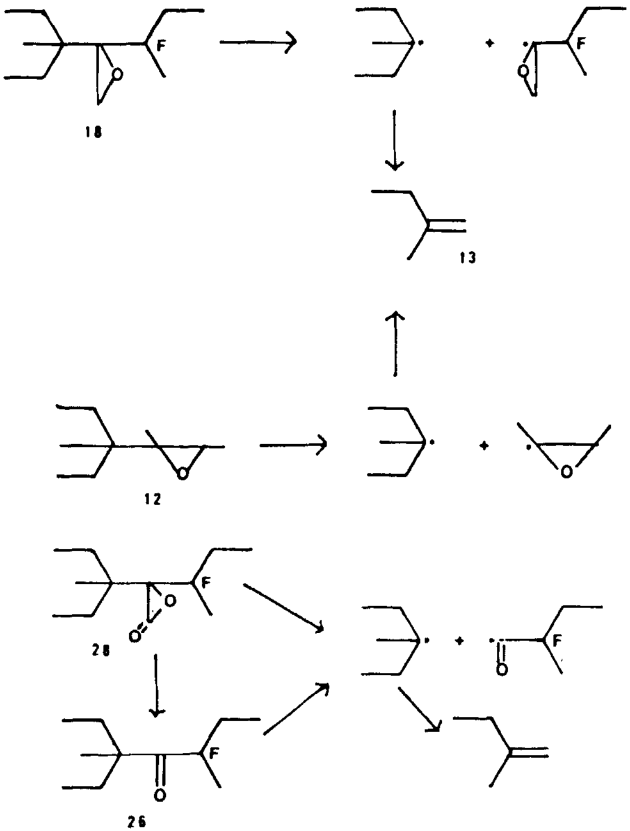
Apparatus.

The flash vacuum thermolysis tube consisted of a quartz tube packed with quartz chippings (40cm x 1.5 cm heated length) mounted horizontally. The temperature was measured by means of a thermocouple at the centre of the heated zone. The sample was introduced by evaporation in vacuo from a heated flask, the vacuum was either by water pump controlled with an Edwards vacuostat or by a high vacuum pump, at the pressures given by individual experiments. The products were



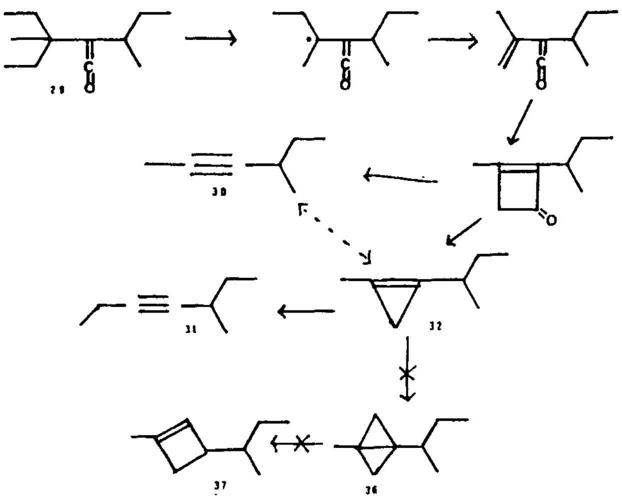
All unmarked bonds joined to fluorine

Scheme 2



All unmarked bonds joined to fluorine

Scheme 3



All unmarked bonds joined to fluorine

Scheme 4

collected in glass traps cooled in liquid air. Analysis of the product mixtures was by gas chromatography using dinonyl phthalate/celite 30/60 mesh 1:3 at 50-80°C. [column A analytical (6' x 1/8" DNP/celite 1:3): column B preparative [30'x 3/8" (DNP/celite 1:3 21')+[30'x 3/8",(DNP/Celite 1:3 21')+(DCEE/Porasil 7')]. ^1H and ^{19}F n.m.r. data for new compounds are shown in Table 1.

Pyrolysis

T.F.E. Pentamer (1) The olefin (10g) was thermolysed at 500° and 15 mm Hg, the reaction was complete in 30 sec. Analysis of the products (6.2g) showed three major components and very minor products. Separation by preparative g.l.c.(column B, 50°) afforded

(i) perfluoro-1,2,3-trimethyl cyclobutene (2) (0.6g)
(ii)E- perfluoro-2,3-dimethylpenta-1,3-diene (3) (1.7g) and
(iii)Z-perfluoro-2,3-dimethylpenta -1,3 diene(4) (2.1g).These were identical to authentic samples [3].

2-Pentafluoroethyl-3,3,4,4,4-pentafluoro-2-trifluoromethyldiazobutane (5) [14]

The diazoalkane (10g) was pyrolysed at 500° and 20mm Hg; the reaction took place over 30 secs. The product (5.2g) was shown to consist of two components. Separation by glc (column B) of a sample (4g) afforded (1) a mixture (2.5g) further separated (column B 50°) to give

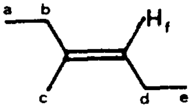
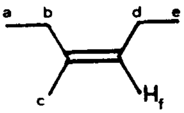
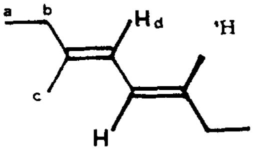
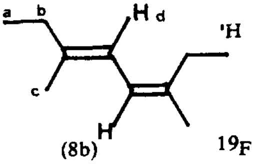
(a) Z- 3H- Perfluoro-4-methylhex-3-ene(6) (1.1g)(nc) bp 124-126°; (b) E-3H-perfluoro -4-methyl hex-3-ene (7) (nc) (1.0g) bp 125-127° (Found for the mixture: C, 25.6; H,0.3% C_7HF_{13} requires C,25.3; H,0.3%), (M.S) m 313 $(M-F)^+$ 263 $(M-CF_3)^+$.
(ii)E/Z -4H,5H - perfluoro-3,6-dimethylocta-3,5-diene (8)(nc) (0.65g) bp 159-161° (Found: C,27.5 H, 0.4% $C_{10}H_2F_{16}$ requires C,28.1; H, 0.4%), (M.S) m 426 $(M)^+$, 357 $(M-CF_3)^+$.

Perfluoro-[2,3-dimethyl-3-(3-methyl-3-pentyl)]azirine (9)

The azirine (9) (10g) was pyrolysed at 500°/20mm to give a mixture (6.4g) separated by glc (column B 50°)to give (i) starting material (1.28g) and
(ii)E/Z-2-cyano-perfluoro-3-methylpent-2-ene (10,11) (nc) (5.1g) bp 79-80° (Found: C,27.5; N 4.9% $C_7F_{11}N$ requires C, 27.4;N,4.6%), (MS) m = 307$(M)^+$, 230$(M-CF_3-H)^+$. By ^{19}F n.m.r. spectroscopy (see Table) the E/Z ratio was 2:3.

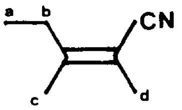
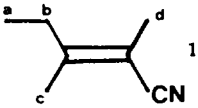
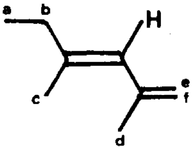
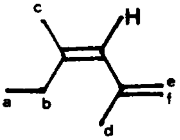
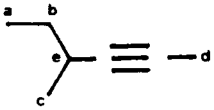
TABLE 1

'H and ^{19}F n.m.r. data

Compound	Chemical shift		Rel Int.	Assignment	Nature of signal
	'H	6.25	(1)	f.	t.J_{fd} = 14Hz
(6)					
	^{19}F	−69	3	c	c
		−86.8	3	a	c
		−88.8	3	e	c
		−115.8	4	b,d	c
	'H	6.40	(1)	f	t.J_{fd} =14Hz
	^{19}F	−67	3	c	c
		−85.5	3	a	c
(7)		−88.7	3	e	c
		−112.0	2	d	c
		−115.8	2	b	c
	'H	7.2	(2)	d	c
(8a)	^{19}F	−59.3	6	c	c Jac 6Hz
		−87.0	6	a	c
		−115.8	4	b	cqJ_{bc} 11Hz
	'H	7.35	(2)	d	c
(8b)	^{19}F	−66.8	6	c	c
		−87.3	6	a	c
		−113.3	4	b	cqJ_{bc} 11Hz

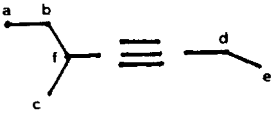
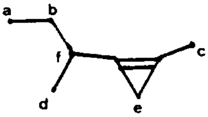
(continued)

TABLE 1 (cont.)

	^{19}F	−57.3	3	d	c
		−58.3	3	c	c
		−81.6	3	a	c
(10)		−109.0	2	b	cq J_{bc} 11.Hz
	^{19}F	−58.3	3	d	c
		59.0	3	c	c
		79.9	3	a	c
(11)		107.4	2	b	c
	'H	6.73	(1)	g	c
	^{19}F	−62.5	3	c	t J_{cb} 25Hz
		−66.3	3	d	c
		−72.8	1	f	c
(24)		−74.5	1	e	c
		−86.5	3	a	c
		−114.1	2	b	c
	'H	−6.4	(1)	g	c
	^{19}F	−63.5	3	d	t J_{cb} 25Hz
		−64.7	3	c	c
(25)		−73.2	1	f	c
		−73.9	1	e	c
		−87.5	3	a	c
		−115.3	2	b	q J_{ab} 25Hz
 (30)	^{19}F	−65.2	3	d	ct
		−74.8	3	c	d J_{de} 15Hz
		−87.7	3	a	c
		−115.0	2	b	cq
		−132.1	1	e	c

(continued)

TABLE I (cont.)

 (31) ^{19}F	-65.0	3	c	c
	-87.3	3	e	c
	-87.6	3	a	c
	-114.8	2	b	c
	-124.1	2	d	d J_{df} 29Hz
	-149.6	1	f	c
 (32) ^{19}F	-78.5	3	c	c
	-83.5	3	d	d J_{df} 13Hz
	-88.9	3	a	c
	-109.2	2	b	c
	-124.5	2	e	AB J_{ab} 282Hz
	-174.4	1	f	c

All unmarked bonds joined to F

Perfluoro[2,3-dimethyl-2-(3-methylpentyl)]oxiran (12)

The oxiran (10g) was pyrolysed at 500°/20mm to give a mixture (5.9g) of (i) perfluoro-2-methylbut-1-ene (13) (3.2g) (ii)perfluoro-2,3-dimethylpent-2-ene (14) (2.6g) both identified by comparison with authentic samples [3].

Perfluoro-2-(1-ethyl-1-methylpropyl)-3-methyl-pent-1-ene. (TFE hexamer) (15)

(a) at 450°. The hexamer (7g) was pyrolysed at 450°/0.4mm to yield a mixture (4.3g) of a clear liquid. Separation by preparative glc (column B 50°) afford (i) perfluoro-1-methyl-2-(1-methylpropyl)-cyclobut-1-ene 1.8g (16) and (ii) E/Z-perfluoro-2-methyl-3-(1-methylpropyl) buta-1,3-diene (1.7g) (17). Both products were identified by comparison with authentic samples [3].

(b) at 590°. In a similar experiment but at 590° the hexamer (7g) afforded a mixture of the cyclobutene (2.5g) and the butadiene (0.9g).

Perfluoro-2-(1-ethyl-1-methylpropyl)-2-(1-methylpropyl) oxiran (18)

(TFE hexamer epoxide.) The oxiran (7g) was pyrolysed at 590°/0.4mm to yield a colourless liquid (2.5g). The liquid was purified from minor components to yield perfluoro-2-methylbut-1-ene (13) identified by comparison with an authentic sample.

Perfluoro-4-ethyl-2,3,4,5-tetramethyl-1,2,3-epoxy-4,5-dihydrofuran (19)

(a) at 440°. The epoxide (5g) was pyrolysed at 440°/0.4mm to yield a pale yellow liquid (4.75g). Analytical glc showed the presence of three major and two minor components. Separation (columnB, 50°) afforded

(i) E/Z perfluoro-3-methylpent-2-ene.(1.7g) (20); (ii) perfluorobiacetyl (0.76g)(21);

(iii) starting material (1.25g) (19)

(iv) E/Z perfluoro-3,4-dimethylhexe-3-en-2-one (0.076g)

These were all identified by comparison with authentic samples.

(b) at 550°. The epoxide (7g) was pyrolysed at 550/0.4mm to give a yellow liquid (5.1g). Separation of a portion (3g) afforded (i) E/Z perfluoro-3-methylpent-2-ene (1.9g) (ii) perfluorobiacetyl (0.9g), both identified by comparison with authentic samples.

4H- Perfluoro-3,5-dimethyl-5-ethylhept-3-ene (23)

The olefin (10g) was pyrolysed at 560°/0.4mm to give a colourless liquid (6.0g). Separation (column B 50°) of a sample (3g) gave (i) a colourless liquid a mixture of very volatile materials (0.12g) not investigated further

(ii) Z-3H - perfluoro-2,4-dimethylhexa-1,3-diene (24) (nc) (1.71g) bp 86- 87°; (Found(for the E/Z mixture): C,27.7; H,0.2; F,72.1 % C_8HF_{13} requires C,27.9; H, 0.3: F, 71.8%) (MS) m 344 $(M)^+$, 325 $(M-F)^+$, 275 $(M-CF_3)^+$;

(iii) E-3H-perfluoro-2,4-dimethylhexa-1,3-diene (25) (nc) (0.86g) bp 86-87°, MS m 344 $(M)^+$, 275 $(M-CF_3)^+$.

Perfluoro-3,5-dimethyl-3-ethylheptanone (26)

The ketone (7g) was pyrolysed at 550°/0.4mm to give a colourless liquid (3.5g). Separation (column B 50°) afforded (i) perfluoro-2-methylbut-1-ene (13) (1.8g); (ii) perfluoro-2-methylbutane (27) (1.1g), MS m 269 $(M-F)^+$, 219 $(M-CF_3)^+$.

Perfluoro-[(1-ethyl-1-methylpropyl)(1-methylpropyl)]ethanolide (28)

The ethanolide (7g) was pyrolysed at 55°/0.4mm.The products (4.1g) were shown by separation to be (i) perfluoro-2-methylbutene (13) (2.4g) and (ii) perfluoro-2-methylbutane (1.69g) (27) identical with authentic samples[3].

Perfluoro-[(1-ethyl-1-methylpropyl)(1-methylpropyl)]keten (29)

The keten (7g) was pyrolysed at 560°/0.4mm to give a colourless liquid (4.03g). Separation (column B 50°) afforded (i) perfluoro-4-methylhex-2-yne (30) (nc) (2.46g) bp 68-69°. The compound was too volatile for accurate elemental analysis; MS m 293 $(M-F)^+$, 262 $(M-CF_2)^+$, 243 $(M-CF_3)^+$, 193 $(M-C_2F_5)^+$; i.r. 2000cm $^{-1}$ (-C≡C-):

(ii) perfluoro-5-methylhept-3-yne (31) (nc) (0.81g) bp 79-80° MS m 326 $(M)^+$, 343 (M-F), 293 $(M-CF_3)$, 243 $(M-C_2F_5)^+$; i.r. 2010 cm^{-1} (-C≡C):

(iii) perfluoro-1-(1-methylpropyl)-2-methylcyclopropene (32) (nc) (0.4g) (0.4g) bp 44-45° MS m 343 $(M-F)^+$, 293 $(M-CF_3)^+$, 243 $(M-C_2F_5)^+$; i.r. 1750cm^{-1} (-C=C-).

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