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REACTIONS OF TETRAFLUOROETHENE OLIGOMERS. PART 4. SOME REACTIONS OF THE MAJOR HEXAMER OLIGOMER WITH NUCLEOPHILES BASED ON OXYGEN AND SULPHUR

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SUMMARY

The major hexamer oligomer of tetrafluoroethene [perfluoro-2-(1-ethyl-1-methylpropyl)-3-methyl-pent-1-ene] (1) reacted with sodium hydroxide under vigorous conditions to afford perfluoro-[(1-ethyl-1-methylpropyl)(1-methylpropyl)]keten (3). Reaction of (1) with methoxide ion in methanol afforded 4-methoxycarbonyl-heneicosafluoro-3,5-dimethyl-5-ethyl-hept-3-ene (5) whereas reaction with methanol in the presence of triethylamine initially afforded (5), but on further reaction yielded (E,Z)-4H-heneicosafluoro-3,5-dimethyl-5-ethylhept-3-ene (4). Reaction of (1) with potassium-t-butoxide in t-butanol afforded (3) whilst with water/triethylamine (4) was obtained. With ethanethiol and sodium benzylthiolate, respectively, hexamer (1) gave ethyl and benzyl [tricosafluoro-3-ethyl-3-methyl-2-(1-methylpropyl)pent-1-enyl]sulphides (6) and (7). With aqueous potassium cyanide, 1-cyanotricosafluoro-3-ethyl-3-methyl-2-(1-methylpropyl)pent-1-ene (8) was obtained.

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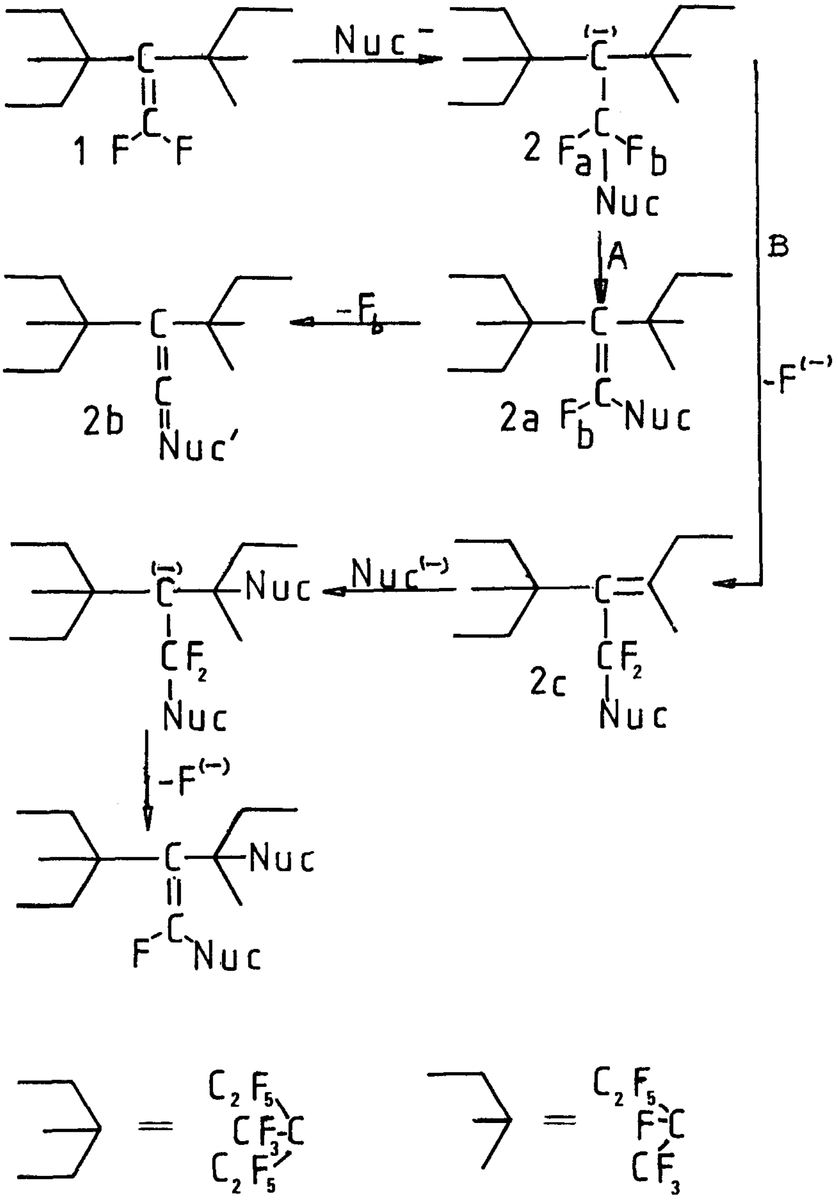
INTRODUCTION

In previous papers in this [1,2] and related series [3,4] we have reported some reactions of the pentamer and the major hexamer oligomers of tetrafluoroethene (TFE) and of some derived compounds. In the present paper, we describe further reactions of the hexamer (1) with a range of nucleophiles mostly centered on oxygen and sulphur, extending the work recently reported involving nucleophiles based on nitrogen [1].

The oligomers [5] of TFE provide an interesting series of compounds for investigations on nucleophilic reactions and our work with the pentamer and hexamer has been parallelled by studies [6] on the tetramer and isomeric alkenes. In each series there is opportunity for loss of fluorine from different positions in the various molecules and possibly further reactions of olefins resulting from fluoride-induced rearrangements of the starting materials [6]. The situation is further complicated by the steric constraints imposed by the bulky perfluoroalkyl groups, which may exercise considerable influence on the reaction pathways

With the major hexamer isomer (1) [See Scheme 1] all these possibilities exist. Clearly, initial attack of the nucleophile will be at the $=CF_2$ end of the double bond [cf. 7] to form the intermediate (2). Loss of fluoride ion could then occur by two pathways: that following the route (A), found to predominate with most fluoroalkenes and cycloalkenes [7], would be by loss of a fluorine from the CF_2 group to give an olefin with one vinyl fluorine (2a). An alternative (B), in our case could be the loss of the tertiary fluorine to give an olefin with no vinylic fluorine (2c). Further reactions are possible: olefin (2a) with a suitable substituent could lose HF or another simple stable fluoride to

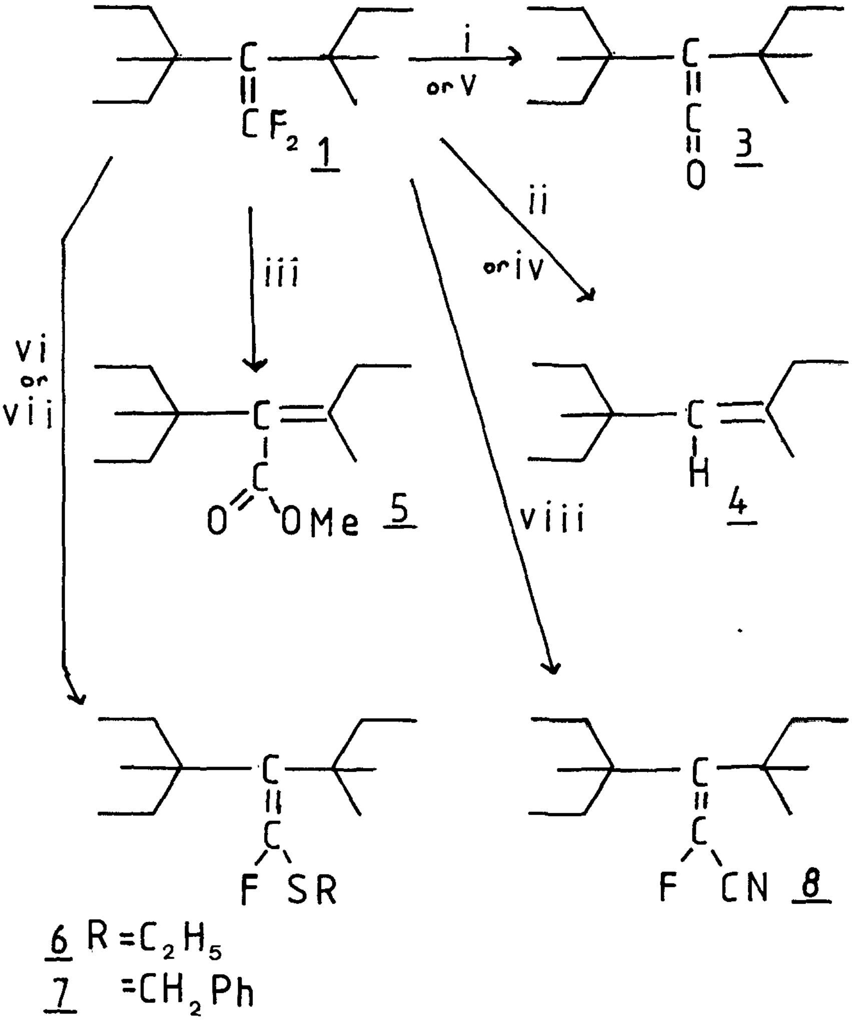


Scheme 1

give a heterocumulene structure (2b). Olefins of all types might react further with nucleophiles to give a complex pattern of polysubstituted products, illustrated for (2c). The picture could be even more complicated by rearrangements induced by fluoride ion, generated by the initial attack of the nucleophile. Such processes have been observed with the less hindered tetramer oligomer [6] and it was of considerable interest to see if they occurred with the highly hindered hexamer (1).

RESULTS

Reactions carried out are summarized in Scheme 2. Water alone is not usually sufficiently nucleophilic to react with fluoroolefins, and hydroxide ion in aqueous bases usually reacts sluggishly in a heterogeneous system (cf. the generation of fluorocycloalkenes with little decomposition from hydrofluorocarbons [8]). Under forcing conditions in co-solvents however reactions of fluoroalkenes with hydroxide ion can lead to extensive decomposition via multiple substitution leading to generation of carbonyl groups, followed by haloform cleavages etc. Hexamer (1) is unusual in that it gives a controlled reaction with aqueous bases affording a keten (3) [9]. In the present work (1) was treated with 10% sodium hydroxide in water, using diglyme as a phase transfer agent. The product, isolated in high yield, had a strong i.r. band at 2160 cm^{-1} typical for heterocumulenes [10]. The ^{19}F n.m.r. spectrum showed the vinylic fluorines to have gone, but that the original fluoroalkyl groups were intact. Therefore, the product was the known [9] keten, perfluoro-[(1-ethyl-1-methylpropyl)(1-methypropyl)keten (3).



(i) NaOH / H_2O / Diglyme; (ii) H_2O / Et_3N / DMF ;

(iii) MeONa/ MeOH: (iv) MeOH/Et_3N ;

(v) t-BuOK / t-BuOH ; (vi) EtSH/Et_2O/ Et_3N ;

(viii) $PhCH_2SNa$/MeOH ; (viii) KCN/H_2O / Diglyme

SCHEME 2

The above reaction is heterogeneous, and in an attempt to obtain keten (3) in a homogenous system we treated hexamer (1) with water in triethylamine/dimethylformamide. A smooth rapid reaction occurred to give a single product in good yield. However, the i.r. spectrum had no band due to the keten (3) and was identical to that of E/Z-4H-heneicosafluoro-3,5-dimethyl-5-ethylhept-3-ene (4) obtained from the reaction of (1) with methanol/triethylamine (see below).

Alkoxides react readily with fluoroolefins [7], and hexamer (1) proved to be no exception. Reaction of (1) with sodium methoxide in methanol afforded a high boiling liquid which appeared to be a single component by glc. The i.r. spectrum showed a strong band at 1770 cm^{-1} and another band at 1665 cm^{-1} attributable at C=O and C=C respectively. The ^{19}F n.m.r. spectrum showed the absence of the olefinic and tertiary fluorines from the original hexamer and indicated the presence of three perfluoroethyl and two trifluoromethyl groups. The ^{1}H n.m.r. spectrum indicated the presence of a single methyl group attached to oxygen. These data suggest the product to be 4-methoxycarbonyl-heneicosafluoro-3,5-dimethyl-5-ethyl-hept-3-ene (5). The material was also obtained from the reaction of the keten (3)with methanol [11].

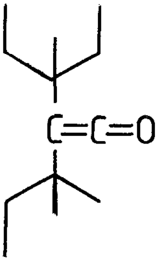
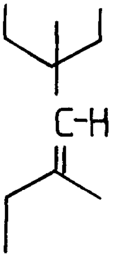
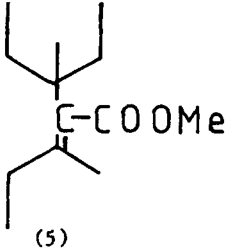
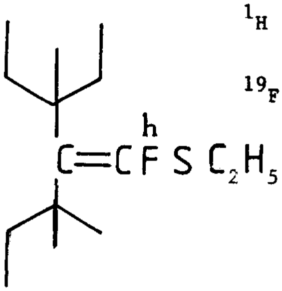
The reactivity of nucleophiles is often altered considerably by changes in the reaction medium, as has been demonstrated by reactions of fluoroolefins with nucleophiles in the presence of tertiary amines [12]. When hexamer (1) was treated with methanol and triethylamine for a short time, the major product was the ester (5), but after a longer period (up to 60 hrs) a new compound was the sole product in good yield. The i.r. spectrum showed that the ester carbonyl group from (5) had disappeared and only a weak absorption at 1660 cm^{-1} was present. The ^{1}H n.m.r. spectrum showed two olefinic proton resonances in the ratio 7:3. The ^{19}F spectrum gave two groups of peaks, in the same ratio, attributable to the same types of fluoroalkyl groups as found in (5). Elemental analysis and mass spectrometry, which indicated a formula $C_{11}F_{21}H$ showed the product to be a 7:3 mixture of E and 4H-heneicosafluoro-3,5-dimethyl-5-ethylhept-3-ene (4), mentioned above and subsequently prepared in another way [11].

Hexamer (1) was treated with potassium-t-butoxide in t-butanol. A rapid reaction occurred affording a single product readily shown to be the keten (3). Variation of the reaction conditions using different ratios of starting materials did not affect significantly the amount of keten (3) formed, only its rate of production. Subsequently [11], we showed that keten (3) did not react under a variety of conditions with t-butoxide/t-butanol systems.

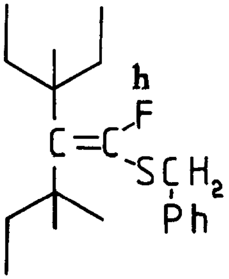
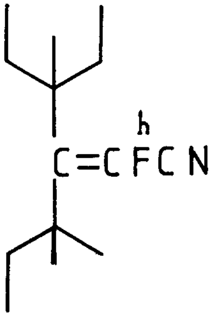
Generally, sulphur compounds exhibit a greater nucleophilicity than their oxygen analogues and this proved to be the case when hexamer (1) was treated with such nucleophiles. Thus, reaction of (1) with ethanethiol proceeded rapidly in ether solution in the present trace of triethylamine and gave a single product which showed one vinylic fluorine in its ^{19}F n.m.r. spectrum as well as the familiar pattern of peaks for the fluoroalkyl groups. ^{1}H n.m.r. spectroscopy showed the presence of an ethyl group attached to sulphur. Mass spectrometry indicated one sulphur atom by isotope ratios, and elemental analysis gave a formula $C_{14}H_5F_{23}S$. Thus, the product was E/Z ethyl[tricosafluoro-3-ethyl-3-methyl-2-(1-methylpropyl)pent-1-enyl]sulphide (6). In a similar reaction sodium benzylthiolate (the less nucleophilic phenylmethanethiol failed to react) afforded the corresponding benzyl analogue (7).

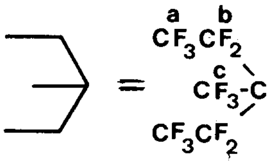
Both sulphides (6 and 7) were heatea in sealed tubes at 120-130°C in an attempt to obtain the thioketen by loss of alkyl fluoride, a method successful with other perfluoro sulphides [13], and which parallels the

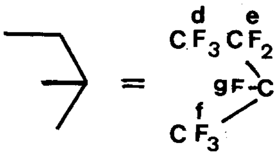
^{1}H and ^{19}F n.m.r. data

Compound	Chemical Shifts			Rel Ints	Assignment	Nature of signal
	^{19}F	57.2		3	c	c
		75.5		3	f	c
		78.8		6	a	c
		80.0		3	d	c
		107.1		4	b	c
		115.5		2	e	CAB
(3)		179.4		1	g	c
		E	Z			
	^{1}H	6.96	6.73			
	^{19}F	58.4	58.4	3	c	c
		61.7	58.4	3	f	c
		79.7	83.2	3	d	c
(4)		79.7	79.7	6	a	c
		108.4	108.4	4	b	c
		106.5	110.1	2	e	c
	^{1}H	3.85				s
	^{19}F	54		3	c	c
		54.9		3	f	c
		73.5		3	d	c
		75.5		6	a	c
(5)		98.8		6	b+e	c
	^{1}H	1.36		3	CH_3	t J=7.2 Hz
		3.00		2	CH_2	q J=7.2 Hz
	^{19}F	52.6		4	c+h	c
		71.8		3	f	c
		77.1		6	a	c
		80		3	d	c
		95.6) 93.5)		4	b	c
		106.5) 111.4)		2	e	c
(6)		170		1	g	c

^{1}H and ^{19}F n.m.r. data

Compound	Chemical Shifts		Rel Ints	Assignment	Nature of signal
	^{1}H	3.94	2	CH_2	s
		7.2	5	Ph	s
	^{19}F	52.8	4	c+h	c
		71.8	3	f	c
		77.1	6	a	c
		79.9	3	d	c
		95.8) 97.8)	4	b	c
		110) 112.5)	2	e	c
(7)		169.5	1	g	c
	^{19}F	55.1-56.4	4	c+h	c
		74-74.6	3	f	c
		79.9	6	a	c
		82.7-83.2	3	d	c
		98 -102	4	b	c
		113-113	2	e	c
		174	1	g	c
(8)					



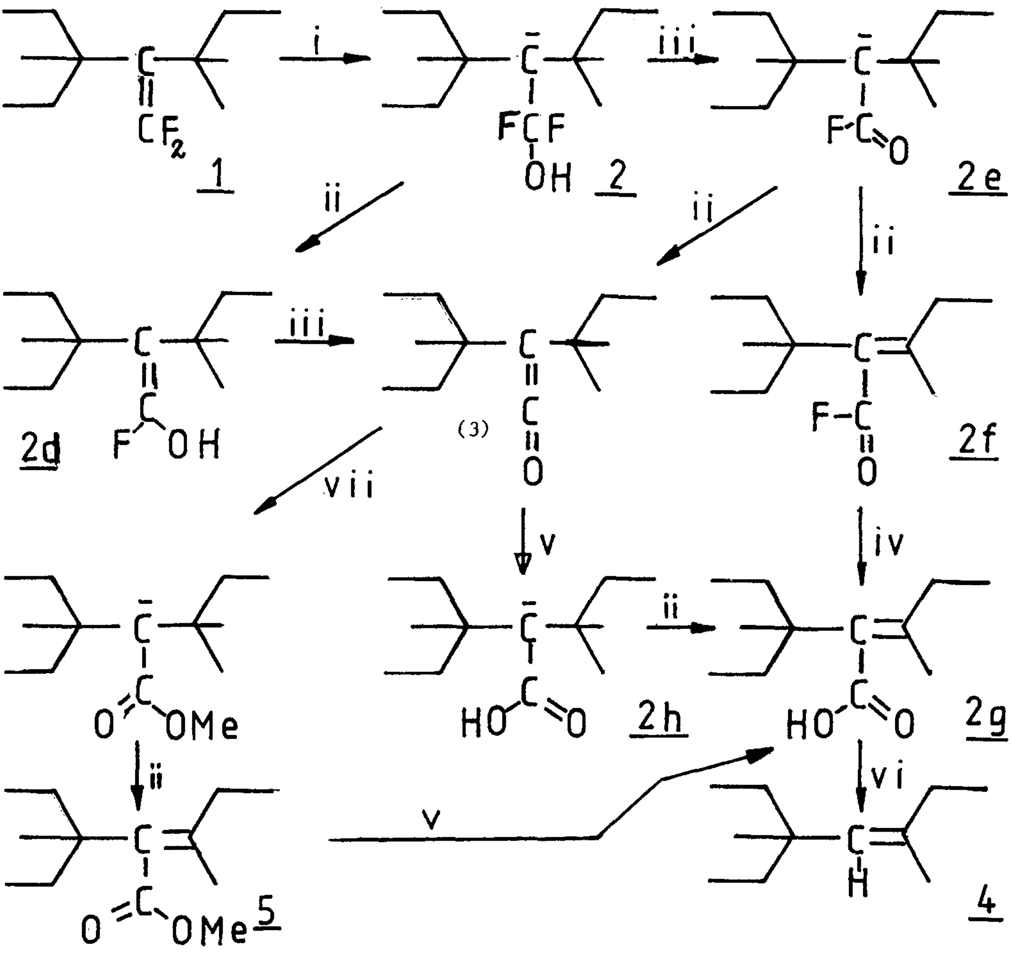


loss of methyl fluoride to give the corresponding keten imine from a dimethyl derivative [1]. No reaction occurred, but at higher temperature there was completed breakdown of the fluorocarbon skeleton to give a complex mixture of products

Reactions of cyanide ion with various fluoroolefins have been carried out, with varying degrees of success: the most common product is an adduct from addition-elimination. When hexamer (1) was treated with potassium cyanide, a slow reaction occurred and a single product was formed. ^{19}F N.m.r spectroscopy indicated a mixture of E/Z isomers with a single vinylic fluorine resonance and the expected peaks due to the fluoroalkyl groups. Infra-red spectroscopy showed the presence of the CN group suggesting that the product was 1-cyano-tricosafluoro-3-ethyl-3-methyl-2-(1-methylpropyl)pent-1-ene (8).

DISCUSSION

These reactions show some interesting and novel mechanistic features. Considering first the reaction of hexamer (1) with water and with alkoxides, it seems fairly certain that the stage 1→2 (Scheme 1) is followed for the initial attack The fate of intermediate 2 then appears to depend on the medium used. When the nucleophile is hydroxide ion (aqueous NaOH) the next possible steps seem reasonably to be those shown in Scheme 3. Loss of $F^{(-)}$ to enol (2 d) can be followed by loss of HF to give keten (3), or loss of HF can occur first to give acid fluoride anion (2e) which then loses fluoride ion to give keten (3). It is known [11] that under the reaction conditions used here, keten (3) does not react with sodium hydroxide It is possible that both of the above pathways can operate.



(i) Add^n of OH$^{(-)}$; (ii) loss of F$^{(-)}$; (iii) Loss of HF catalysed by Et$_3$N ;

(iv) Exchange OH for F ; (v) Add^n of OH$^{(-)}$

(vi) decarboxylation ; (vii) Add^n of Meo$^{(-)}$

SCHEME 3

The reaction with water/triethylamine/DMF follows a different course. Some of the various possibilities are shown in Scheme 3. Firstly, the formation from the ion (2a) of the unsaturated acyl fluoride (2f) could be favoured in the different medium, and this would be followed by its hydrolysis to the acid (2g). This latter would be expected [14, 11] to decarboxylate fairly readily to give olefin (4). Alternatively, the keten (3) could be formed and then activated towards attack by hydroxide by the triethylamine present: an intermediate such as (2h) or a re-arranged anion, would then give acid (2g) and thence the observed olefin (4). The E/Z ratio of olefin (4) from this reaction is 3:1. Recently [11] we have shown that keten (3) reacts under the same conditions with water to give the same olefin in approximately the same ratio, thus supporting the proposal that the keten (3) is an intermediate in the reaction.

In the reaction of (1) with methoxide ion in methanol a double bond shift occurs. It seems unlikely however that an intermediate such as (2c) of Scheme 1 is involved, since further addition to this new double bond might be expected. However, a reasonable explanation can follow if the keten (3) is an intermediate in the reaction sequence; the keten could be formed from an intermediate of type (2a) of Scheme 1 (Nuc=OMe) which could react in two ways. Elimination of methyl fluoride (analogous to loss of HF from 2 d, Scheme 3) would give the keten (3) directly. Alternatively, the intermediate of type 2a (Nuc=OMe) could be attacked by methoxide ion at the methyl group, eliminating dimethyl ether and giving the acyl fluoride anion 2e (Scheme 3) and thence keten (3): such formations of carbonyl groups from alkoxides are known [16]. Methoxylation of the keten (3) would then follow to give the ester (5). Subsequently [11] we have shown in a separate experiment that (3) does react with methanol/methoxide to give the ester (5) in good yield under similar reactions conditions. The reaction with methanol/triethylamine seems at first sight to follow a different course, yielding the olefin (4). We believe however that the pathway follows that described above to yield ester (5) and indeed after a short reaction time (5) can be detected as the major product. The next step in the reaction is the demethylation of (5) by triethylamine to give the corresponding unsaturated acid (2g) which decarboxylates to give (4) (Scheme 3).

The reactions with ethanethiol, phenylmethanethiol and potassium cyanide all follow the expected pattern of reaction at the $CF_2=$ group with loss of fluoride ion to give products of type 2a (Scheme 1).

In the case of the two sulphides, thermolysis failed to yield the thioketen or its dimer in the manner observed by Knunyants [13]. This was a disappointing result. Elimination would have proceeded at higher temperatures, but at those temperatures thermal decomposition of the highly branched fluoroalkyl groups becomes a major factor, in line with previous results [15].

EXPERIMENTAL

Perfluoro [(1-ethyl-1-methylpropyl)(1-methylpropyl)]keten (3)

Sodium hydroxide (16g) in water (160 cm^3) was added over 45 min. to a vigorously - stirred solution of the hexamer (1) (50 g) in diglyme (10 g) at 80°C. The mixture was then stirred at 80-90°C for 18 hr. On cooling, a lower fluorocarbon layer separated and was removed, washed with water and dried ($CaCl_2$). Distillation afforded perfluoro-[(1-ethyl-1-methylpropyl) (1-methylpropyl)]keten (3) (39.6 g) b.p. 165-167°C (Found: C, 24.7, F 72.8. $C_{12}F_{22}O$ requires C, 24.9, F, 72.3%); i.r., 2160 cm^{-1} (C=C=O).

Reactions of hexamer (1) with alcohols and with alkoxides

(a) Sodium methoxide in methanol

The hexamer (6 g) was added to a solution of sodium methoxide in methano (sodium 0.46 g; dry methanol 30 cm^3). The mixture was stirred and refluxed for 5 hr., cooled and water (100 cm^3) added. The fluorocarbon layer was separated, washed, dried and distilled to give 4-methoxycarbonyl-heneicosafluoro-3,5-dimethyl-5-ethylhept-3-ene (nc) (5) (4.6 g), identical to an authentic sample [11].

(b) Methanol/triethylamine

The hexamer (10 g) was added to a solution of dry triethylamine (10 cm^3) in dry methanol (30 cm^3) and the mixture stirred at 18°C for 2 hr. A small sample of the lower fluorocarbon layer was shown by i.r. and n.m.r. spectroscopy to be mainly ester (5). Stirring was continued for 60 hr. at 18°C when water (100 cm^3) was added. The lower fluorocarbon layer (7.2 g) was separated and dried ($CaCl_2$). Distillation afforded EZ 4H-heneicosafluoro-3,5-dimethyl-5-ethylhept-4-ene(4) (nc) (6.8 g), b.p.145°C (Found: C, 25.0; H, 0.4; F, 74.6%. $C_{11}HF_{21}$ requires C, 24.8; H, 0.2; F, 75.0%); ^{19}F n.m.r. spectroscopy showed the E/Z ratio as 7:3.

(c) Potassium-t-butoxide/t-butanol

A solution of potassium-t-butoxide (1 M) in t-butanol (100 cm^3) was added to a stirred suspension of the hexamer (9.5g) in t-butanol (20 cm^3). A brown colour quickly developed, and stirring was continued for 30 min. Water (250 cm^3) was added and the lower fluorocarbon layer was separated to give the keten (3) (4.5g). In similar experiments using different ratios of hexamer to t-butoxide, the keten (3) was formed but at slower rates.

Reaction with water/triethylamine/dimethylformamide

A mixture of hexamer (60g), triethylamine (10g) water (2g) and dimethylformamide (65 cm^3) were heated and stirred at 75°C for 7 hr. On cooling, the lower fluorocarbon layer was separated and dried to yield on distillation E/Z-4H-heneicosafluoro-3,5 dimethyl-5-ethylhept-3-ene(4) (26.6g),(E/Z ratio 3:1 by n.m.r. spectroscopic analysis) identical to an authentic sample.

Reaction with ethanethiol

Ethanethiol (10 cm^3) in dry ether (50 cm^3) was added to hexamer (24g) in ether (100 cm^3) with stirring. Triethylamine (20 cm^3) was added, a yellow colour developed and the hexamer dissolved to give a one phase system. After being stirred for three hours the most volatile materials were removed in vacuo. Distillation of the residue at 0.2 mmHg pressure afford (EZ) ethyl[tricosafluoro-3-ethyl-methyl-2-(1-methylpropyl)-pent-1-enyl]sulphide (nc) (6) (16.7g) b.p. 53-58°C (0.2mm) (Found: C, 26.0; H, 0.7; F, 68.1; S, 5.2. $C_{14}H_5F_{23}S$ requires C, 26.2; H, 0.8, F, 68.0; S 5.0%).

Reaction with phenylmethanethiol

Sodium benzylthiolate (from phenylmethanethiol 5.5 cm^3 and sodium 1g) in dry methanol (25 cm^3) was added dropwise to a solution of hexamer (24g) in dry ether (100 cm^3). The mixture was heated under reflux for 4 hr, the volatile materials were evaporated and water (100 cm^3) was added to the residue. The lower layer was separated off, washed with methanol (50 cm^3) and dried ($CaCl_2$). The residue was distilled in vacuo to give benzyl [tricosafluoro-3-ethyl-3-methyl-2-(1-methylpropyl)pent-1-enyl]sulphide (nc) (7) (5.8g)b.p. 118°/0.2mmHg (Found: C, 32.5; H, 0.8; F, 62.5; S, 4.6. $C_{19}H_7F_{23}S$ requires C, 32.4; H, 1.0; F, 62.0; S 4.6%).

Reaction with potassium cyanide

Hexamer (12 g) was added to a solution of potassium cyanide (3.3 g) in wate ($50\ cm^3$) containing diglyme ($2\ cm^3$) as phase transfer catalyst. The mixture was heated and stirred at 100° for 5 hrs and then cooled and continuously extracted with ether for 40 hr. The dried ($MgSO_4$) ether extract was distilled to give two layers, the upper diglyme layer was discarded and the lower fluorocarbon layer (6.1 g) was shown by analytical glc to be a mixture of two components. Separation of a portion (0.5 g) by preparative glc afforded (1) hexamer (0.16 g) and (ii) 1-cyanotricosafluoro-3-ethyl-3-methyl-2-(1-methylpropyl)pent-1-ene(nc)(8) (0.18 g) b.p. 188°C (Found; C, 25.4; F, 72.4; N, 2.5. $C_{13}F_{23}N$ requires: C, 25.7; F, 72: N, 2.3%), as a mixture of E and Z isomers.

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