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REACTIONS OF TETRAFLUOROETHENE OLIGOMERS. PART 5. SOME REACTIONS OF PERFLUORO-[(1-ETHYL-1-METHYLPROPYL)(1-METHYLPROPYL)] KETEN

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SUMMARY

The title keten (1) was treated with some alcohols and amines: methanol afforded an inseparable mixture of two products, 4H-4-methoxycarbonyl-docosafluoro-3,5-dimethyl-3-ethylheptane (2) and 4-methoxycarbonyl-heneicosafluoro-3,5-dimethyl-5-ethylhept-3-ene (3). Treatment of the mixture with sodium hydroxide afforded pure (3). Reaction of (1) with benzyl alcohol yielded 4-benzyloxycarbonyl-4H-docosafluoro-3,5-dimethyl-3-ethylheptane (4) which on hydrogenation gave a mixture of 4H-heneicosafluoro-3,5-dimethyl-5-ethylhept-3-ene (5) and 4H-docosafluoro-3,5-dimethyl-3-ethyl-heptane-4-carboxylic acid (6). Reaction of (1) with ammonia yielded 4-carbonamido-heneicosafluoro-3,5-dimethyl-5-ethylhept-3-ene (7) and dimethylamine similarly afforded the N,N-dimethyl analogue (9). However, reaction of (1) with ethylamine gave an unusual cyclisation product, 1-ethyl-3H-heneicosafluoro-4-ethyl-4-methyl-3(1-ethyl-1-methylpropyl)azetan-2-one (8).

INTRODUCTION

Perfluoro-[(1-ethyl-1-methylpropyl)(1-methylpropyl)] keten (1) is easily obtained from the major hexamer oligomer of tetrafluoroethene [1]. It is one of the relatively few ketens readily available for study which exist in the monomeric form. The reactions of those that are known have

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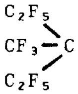
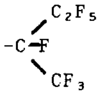
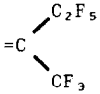
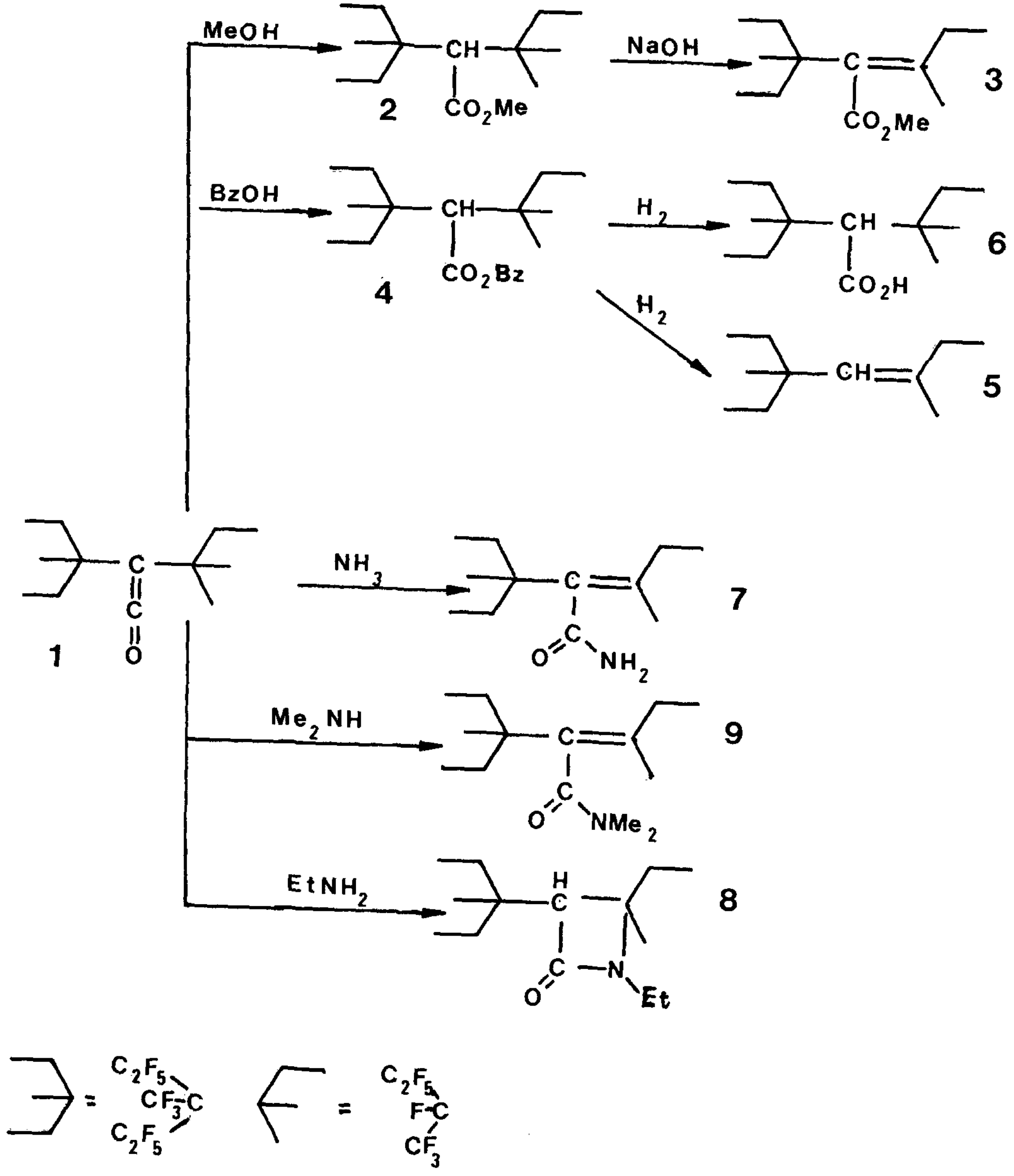
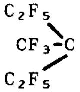
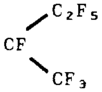
been well reviewed [2], and generally fall into two groups; nucleophilic attack at the carbonyl group, and cyclo-addition reactions. In fluorine chemistry, most attention has been focussed on bis(trifluoromethyl) keten and its reactions have been widely studied [3]. The formation of the 'hexamer ketene' (1) was first described in the patent literature [4] and again in the previous part of this series [1]. We also reported the formation of a stable α-lactone by reaction of (1) with sodium hypochlorit [5]. We now report some reactions of (1) with nucleophiles (see Scheme 1)

RESULTS

The keten (1) was treated with dry methanol under reflux, the reaction at room temperature being very slow, to give a mixture of two products (2 and 3) which could not be separated either by distillation or by chromatographic techniques. ^1H and ^{19}F n.m.r. spectroscopy and i.r. spectroscopy indicated that both compounds were methyl esters, and that both contained a  $CF_3-C(C_2F_5)_2$ group. However, a  $-CF(C_2F_5)(CF_3)$ group was also present in one and a  $=C(C_2F_5)(CF_3)$ group in the other, the latter involving the formation of a double bond with loss of the tertiary fluorine atom. Further, one compound contained a single proton on a carbon bearing the ester function. The integral ratios of the peaks showed a 1:1 mixture. Treatment of the mixture with sodium hydroxide in aqueous diglyme gave a single component, identical to one of the original compounds, in good yield. The ^{19}F and ^1H n.m.r. spectra showed the mixture to have lost the single proton and the tertiary fluorine atom, but the ester group had remained intact. These data, along with mass spectrometry and elemental analysis confirmed the final product to be 4-methoxycarbonyl-heneicosafluoro-3,5-dimethyl-5-ethylhept-3-ene (3). By inference, the other component in the original mixture was methanol addition product, 4H-4-methoxycarbonyl-docosafluoro-3,5-dimethyl-3-ethylheptane (2). Further evidence for this structure came from the reaction with benzyl alcohol. The keten (1) and benzyl alcohol were heated together at 150°C, and in a relatively slow reaction a single component was obtained. The ^{19}F n.m.r. spectrum showed a similar pattern to that adduced for (2), after deletion of the peaks associated with compound (3), i.e. the presence of


MeOH
CH
CO_2Me
2
NaOH
C
CO_2Me
3
BzOH
CH
CO_2Bz
4
H_2
CH
CO_2H
6
H_2
CH
5
C
C
O
1
NH_3
C
C
O
NH_2
7
Me_2NH
C
C
O
NMe_2
9
$EtNH_2$
H
C
C
O
N
Et
8
C_2F_5
CF_3-C
C_2F_5
=
C_2F_5
F-C
CF_3
=

SCHEME 1

 and  groups was established, whilst a peak in the ^{1}H n.m.r. spectrum at *ca.* 4.9 δ was attributable to a proton on a carbon bearing a CO_2R group, peaks due to the $PhCH_2$ group being present also. Thus, the product can be identified as 4H-4-benzyloxycarbonyl-docosafluoro-3,5-dimethyl-3-ethylheptane (4).

Removal of benzyl groups from the corresponding esters and ethers by catalytic hydrogenation is well established during protection of oxygen functions, and hydrogenation of (4) was an obvious route to the corresponding carboxylic acid, though with reservations about ready decarboxylation. When ester (4) was hydrogenated under one atmosphere pressure of hydrogen using palladium on carbon as the catalyst, followed by work up avoiding heat and basic conditions, a colourless liquid was obtained. Slow distillation *in vacuo* without heating gave two fractions, a more volatile liquid and a waxy solid. The liquid was shown to be E/Z-4H-heneicosafluoro-3,5-dimethyl-5-ethylhept-3-ene (5), a compound formed from other reactions of the hexamer oligomer [1]. The waxy solid showed a broad band in the region 3500-2700 cm^{-1} in its i.r. spectrum and a very strong band at 1760 cm^{-1} typical of a carboxylic acid. It was found to be very difficult to obtain n.m.r. spectra of this compound because of ready loss of carbon dioxide from the material in solution.

This problem was eventually solved by running the spectrum of a melt in a micro-tube at 50°C. The resulting peaks due to proton and fluorine were consistent with the material being 4H-docosafluoro-3,5-dimethyl-3-ethyl-heptane-4-carboxylic acid (6). The yield of the acid was low (13%) and the major product was the olefin (5). The n.m.r. experiments confirmed our views that the acid (6) does readily decarboxylate, and this has prevented any further study of its reactions.

An alternative method of obtaining the acid could be the acid hydrolysis of either the benzyl ester or the tert-butyl ester. We found that under normal reaction conditions, ester (4) was unaffected by acids. Thus, we attempted to prepare the tert-butyl ester by reaction of the keten (1) with t-butanol or potassium or sodium t-butoxide. Under a variety of conditions no reaction took place, presumably a reflection of the steric constraints imposed on the system by all the bulky groups present. This result parallels that we have reported previously [1] on the reaction of the hexamer oligomer with t-butanol.

TABLE

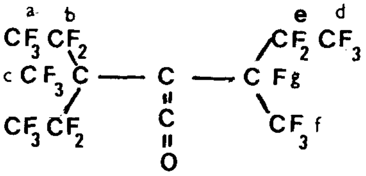
^{19}F and ^{1}H n.m.r. data

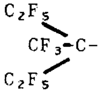
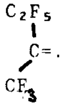
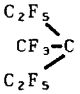
Compound		Chemical Shifts	Rel. Intensity	Position	Type of Signal/ Coupling
1	F	57.2	3	c	c
		75.5	3	f	c
		78.8	6	a	c
		80	3	d	c
		107.1	4	b	c
		115.5	2	e	CAB overlapping
		179.4	1	g	c
2	F	57.3	3	c	c
		74.9	6	a	c
		75.5			
		77.2	3	f	c
		80	3	d	c
		99.5	4	b	c
		101.3			
		109-112	2	e	c
		171	1	g	c
	H	3.76	3	OMe	s
		4.88	1	CH	s
3	F	54	3	c	c
		54.9	3	f	c
		73.5	3	d	c
		75.5	6	a	c
		98.8	6	b+e	c
	H	3.85	(3)	OMe	s
4	F	57.5	3	c	c
		74.5	6	a	c
		77.3			
		75.3	3	f	c
		79.9	3	d	c
		99.8	4	b	c
		101.0			
		110.5	2	e	c
		171.5	1	g	c
	H	4.93	1	CH	s
		5.09	2	$-CH_2Ph$	s
		7.28	5	Ph	s
5	E (isomer)				
	F	58.4	3	c	c
		61.7	3	f	c
		79.7	3	d	c
		79.7	6	a	c
		108.4	4	b	c
		106.5	2	e	c

(Continued)

TABLE (cont.)

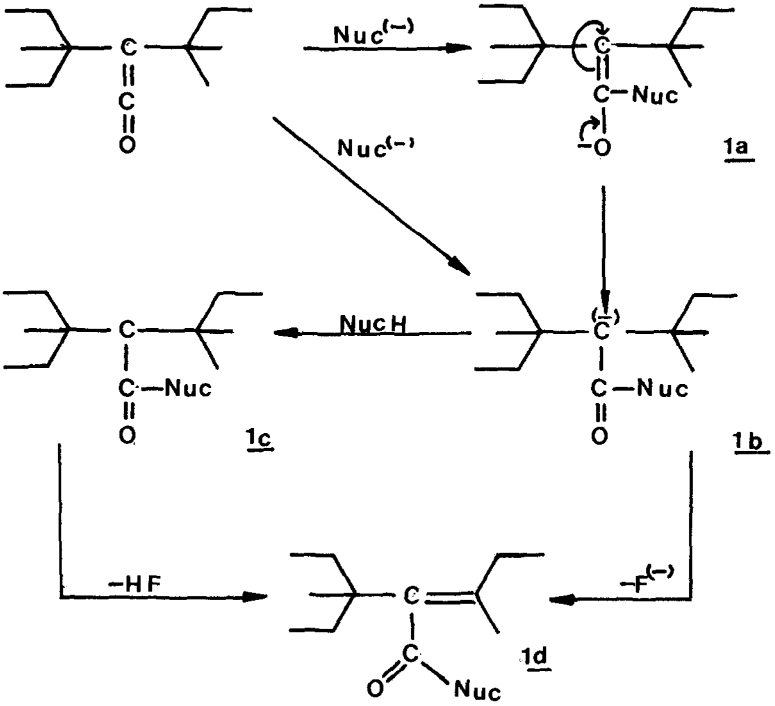
	H	6.96	(1)	=C-H	s
5	Z (isomer)				
	F	58.4	3	c	c
		58.4	3	f	c
		83.2	3	d	c
		79.7	6	a	c
		108.4	4	b	c
		110.1	2	e	cq J_{ef} 11 Hz
	H	6.73	(1)	=C-H	s
7	F	52.5	3	c	c
		53.4	3	f	c
		72.9	3	d	c
		75.6	6	a	c
		98.5	6	b+e	c
	H	7.82	(2)	$-NH_2$	bs
9	F	54.4	3	c	c
		55.7	3	f	c
		73.4	3	d	c
		75.7	6	a	c
		94.6	2	e	c
		98.5	4	b	c
	H	2.96	(6)	NMe_2	s
8	F	61.5	3	c	c
		66.2	3	f	c
		79.0	6	a	c
		81.5	3	d	qJ_{df}=5Hz
		105.7 107.2	4	b	c
		115.0	2	e	CAB J_{AB}=290Hz $\Delta\nu AB$=250Hz
	H	1.2	3	$CH_2\underline{CH_3}$	t
		3.32	2	$\underline{CH_2}CH_3$	c
		4.60	1	CH	s



In a rapid reaction of keten (1) with ammonia in ether, an oil was formed which slowly crystallised to a pale yellow solid. The ^1H n.m.r. spectrum showed a proton signal which disappeared on shaking the sample with D_2O. The ^{19}F spectrum indicated the presence of the groups  $(C_2F_5)_2(CF_3)C-$ and  $(C_2F_5)(CF_3)C=$. The i.r. spectrum showed the presence of absorptions typical of an $\alpha\beta$-unsaturated amide. Thus, we concluded that the product was 4-carbo-amido-heneicosafluoro-3,5-dimethyl-5-ethylhept-3-ene (7). In a similar reaction, dimethylamine afforded the corresponding N,N-dimethyl derivative (9). However, reaction of the keten (1) with ethylamine afforded an entirely different product. The reaction produced a bright yellow oil which on examination by i.r. spectroscopy showed a very strong band at 1820 cm^{-1}. This is a high value for a carbonyl or carboxyl group, but compares with some other C=O absorptions noted in four membered rings containing perfluoroalkyl groups [6]. The ^{19}F n.m.r. spectrum showed the presence of the  $(C_2F_5)_2(CF_3)C$ group, signals for two CF_3- groups and one CF_2 group: no signals for a tertiary fluorine atom were observed. The ^1H n.m.r. spectrum indicated a C_2H_5 group attached to nitrogen, and a signal due to a single proton at 4.6 δ, attributable to a proton in a four membered ring next to a C=O group [cf. 6]. These data suggest to us that the product is 1-ethyl-3H-heneicosafluoro-4-ethyl-4-methyl-3-(1-ethyl-1-methylpropyl)azetan-2-one (8).

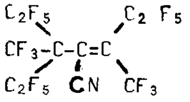
DISCUSSION

From the results obtained it is clear that the keten (1) reacts initially at the carbon atom of the carbonyl group with the nucleophiles we have studied. As indicated in Scheme 2, this may be by formation of a carbanion (1b) which then protonates to give a saturated product (1c) and/or loses fluoride ion to give an alkene (1d). Subsequent loss of hydrogen fluoride from (1c) also affords (1d). It would appear that with the more basic reagents (NH_3, Me_2NH and $EtNH_2$), elimination to give products of the structural type (1d) occurs. With methanol a mixture of both types (1c) and (1d) is obtained, whereas the less basic benzyl alcohol leads only to a product of type (1c).



Scheme 2

It is possible that the first anionic intermediate is actually a resonating species, with the major contributors as (1a) and (1b). The present reagents could all give more stable products with form (1b).

The cyclisation to give the azetanone (8) was slightly surprising in view of the straight forward reactions with ammonia where we found no evidence for further reaction. The reaction of ammonia with TFE hexamer, first gives  $CF_3-C(C_2F_5)_2-C(CN)=C(C_2F_5)CF_3$ which then reacts further with ammonia [7]). This change in reactivity may be some extent be reflected in the degrees of activation of the double bond by CN, $CONH_2$ and CONHEt. Cyclisations of this type have previously been observed by Chambers [8] and by ourselves [9] in some recent work.

EXPERIMENTAL

Reaction of keten (1) with methanol. The keten (6.0 g) [4] and dry methanol (30 cm^3) were heated under reflex for 1 hr. On cooling, the mixture separated into two layers. The lower fluorocarbon layer (5.9 g) appeared by g.l.c. to be one component, but on examination by ^{1}H and ^{19}F n.m.r. spectroscopy the product was shown to be a mixture of two compounds in equal proportions. Analysis of the spectra indicated the two components to be 4H-4-methoxycarbonyl-docosafluoro-3,5-dimethyl-3-ethylheptane (2) and 4-methoxycarbonyl-heneicosafluoro-3,5-dimethyl-5-ethylhept-3-ene (3) (see below).

Dehydrofluorination of the mixture of esters (2) and (3). The mixture above (4.0 g) was refluxed with sodium hydroxide (3.2 g) in water (20 cm^3) and diglyme (3 cm^3). After 30 mins. the mixture was poured into water (50 cm^3) and the fluorocarbon layer separated to give 4-methoxycarbonyl-heneicosafluoro-3,5-dimethyl-5-ethylhept-3-ene (3) (nc) (1.36 g) b.p. 85°C (12 mm Hg) (Found: C, 26.4; H, 0.6; F, 67.1. $C_{13}H_3F_{21}O_2$ requires: C, 26.5; H, 0.5; F, 67.6%) i.r. 1770 cm^{-1} C=O.

Reaction of keten (1) with benzyl alcohol. The keten (40 g) and benzyl alcohol (150 g) were heated together at 150°C for 30 hrs. On cooling ethanol (150 cm^3) was added, the fluorocarbon layer separated and washed with water. The dried ($MgSO_4$) layer was distilled in vacuo to yield 4-benzyloxycarbonyl-4H-docosafluoro-3,5-dimethyl-5-ethylheptane (4) (nc) (26.3 g), b.p. 150-160°C (12 Mm Hg) (Found: C, 33.0; H, 1.4; F, 61.4. $C_{19}H_8F_{22}O_2$ requires: C, 33.3; H, 1.2; F, 60.9%) i.r. 1780 cm^{-1} C=O.

Hydrogenation of ester (4). The ester (4) (8 g) in dry ether (25 cm^3) was shaken in an atmosphere of hydrogen with palladium 10% on carbon (0.03 g). After 3 hrs., no more hydrogen was absorbed. The catalyst was filtered off and the solvent removed to yield a colourless liquid (6.0 g). Distillation in vacuo afforded two fractions:- (i), 4H-heneicosafluoro-3,5-dimethyl-5-ethylhept-3-ene (5) (nc) (5.0 g), b.p.

145°C; identical to an authentic specimen [1]; ^{19}F n.m.r. spectroscopy indicated a E/Z isomer mixture in the ratio 7:3 : (ii), 4H-docosafluoro-3,5-dimethyl-3-ethylheptane-4-carboxylic acid (6) (nc) (0.9 g), m.p. 36-38°C (Found: C, 24.3; H, 0.3; F, 70.4. $C_{12}F_{22}H_2O_2$ requires C, 24.2; H, 0.3; F, 70.1%) i.r. 1760 cm^{-1} C=O, 3500-2700 broad OH.

Reaction with ammonia. The keten (1) (5.5 g) was added to a stirred saturated solution of ammonia in dry ether (100 cm^3) at 0°C, during ten minutes. The mixture was then stirred for 1.5 hrs. at 0°C. The precipitated ammonium fluoride was filtered off and the ether evaporated to leave an oily residue. Distillation in vacuo afforded 4-Carbonamido-heneicosafluoro-3,5-dimethyl-5-ethylhept-3-ene (7) (nc) (2.4 g), b.p. 95°C/0.5 mm which crystallised to a yellow solid m.p. 82°C (Found: C, 25.5; H, 0.2; F, 68.9; N, 2.5. $C_{12}H_2F_{21}NO$ requires C, 25.2; H, 0.4; F, 69.4; N, 2.4%) i.r. 3540 and 3440 cm^{-1} NH_2 1710 cm^{-1} C=O.

Reaction with ethylamine. The keten (15 g) was added over ten minutes to ethylamine (10 cm^3) in dry ether (100 cm^3) at 0°. The mixture was stirred for 2 hrs. at 0°C, and then for 15 hrs. at 18°C. The solvents were evaporated to yield a yellow oil (12.5 g). Distillation in vacuo afforded 1-ethyl-3H-heneicosafluoro-4-ethyl-4-methyl-3-(1-ethyl-1-methylpropyl) azetan-2-one (8) (nc) (8.0 g), b.p. 57°C/0.05 mm. Found: C, 28.1; H, 1.3; F, 66.6; N, 2.3. $C_{14}H_6F_{21}NO$ requires C, 27.9; H, 1.0; F, 66.2; N, 2.3 %).

Reaction with dimethylamine. The keten (11 g) was added over ten minutes to a stirred solution of dimethylamine (10 cm^3) in dry ether (100 cm^3) at 0°C. The mixture was stirred at 0°C for one hour and then at 18°C for three hours. The precipitated ammonium fluoride was filtered off and the solvents evaporated to leave an orange-coloured residue (8.3 g). Distillation in vacuo afforded 4-(N,N-dimethyl-carbonamido)-heneicosafluoro-3,5-dimethyl-5-ethylheptene (9) (nc) (5.2 g), b.p. 65-70°C/0.05mm. (Found: C, 27.9; H, 1.1; F, 66.5; N, 2.5. $C_{14}H_6F_{21}NO$ requires C, 27.9; H, 1.0; F, 66.2; N, 2.3 %).

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