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POLYFLUOROCYCLOALKENES. PART XVII. FURTHER PREPARATIONS OF ALKOXY-NONAFLUOROCYCLOHEXENES AND THEIR PYROLYSES TO POLYFLUOROCYCLOHEX-2-ENONES

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SUMMARY

Reactions between decafluorocyclohexene and substituted ethanols ($HOCH_2CH_2X$: X = Cl, Br, I, and OMe) gave, in each case, a mixture of the corresponding 1- and 3-alkoxy-nonafluorocyclohexene (roughly 3:1). Pyrolysis of the 1-(2-methoxyethoxide) over glass or alumina at 520°C gave octafluorocyclohex-2-enone. This was obtained also in good yield by pyrolysis of the known 1-ethoxy- and 1-(2-acetoxyethoxy)- analogues. From the other 1-alkoxides the same enone was formed, but accompanied by other products: from the 1-(2-bromoethoxide), nonafluorocyclohex-1-enyl vinyl ether and 3-bromoheptafluorocyclohex-2-enone; from the 1-(2-chloroethoxide), the vinyl ether and 2-chloroheptafluorocyclohex-2-enone; from the 1-(2-iodoethoxide) at 395°C, 6,6,7,7,8,8,9,9-octafluoro-2-oxabicyclo[4,3,0]-nona-1(5),3-diene. Pyrolyses at lower temperatures gave much unreacted 1-alkoxides, but no rearrangement to 3-alkoxides was detected. In contrast, the 3-ethoxy- and 3-(1-bromoethoxy)-isomers decomposed to a greater extent at 390°C, to give the octafluoroenone, but, besides unreacted starting materials, some isomeric 1-alkoxide was present in each case. Reaction of octafluorocyclohex-2-enone with chlorides and bromides gave the respective 3-chloro- and 3-bromo-2-enones, whilst with base, a haloform cleavage took place within the conjugated system to give cis-6H-octafluorohex-5-enoic acid.

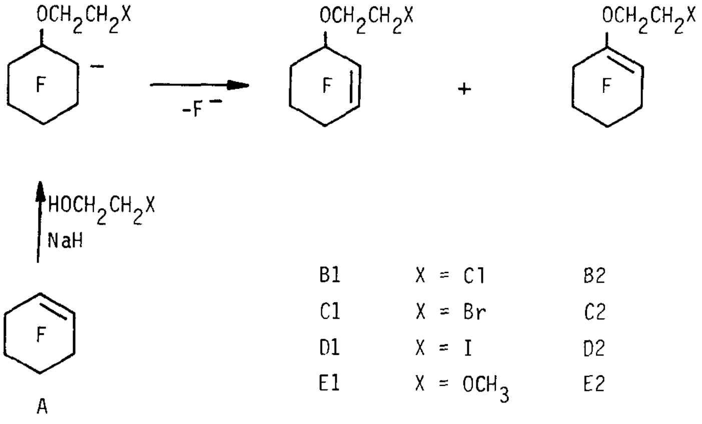
INTRODUCTION

Additions to perfluorocyclohexenes are of continuing interest [1], and syntheses of nonafluorocyclohex-1- and -3-enyl ethers by nucleophilic reactions with alcohols were carried out long ago [2]. Subsequently, further ionic additions to decafluorocyclohexene of alcohols containing a second functional group were reported [3], and reactions of the ether products studied. This paper extends this approach to four other derivatives of ethanol. Further, the derived new alkoxides and other known ethers were subjected to pyrolysis reactions to determine whether useful synthetic approaches could be developed. Octafluorocyclohex-2-enone was a universal product, and is quite readily available using this approach.

RESULTS AND DISCUSSION

Alkoxy-nonafluorocyclohexenes

Reactions of the alcohols with decafluorocyclohexene (Scheme 1) were promoted by sodium hydride [3] rather than potassium hydroxide [*cf*. 2].



B1 $X = Cl$ B2
C1 $X = Br$ C2
D1 $X = I$ D2
E1 $X = OCH_3$ E2

Scheme 1

From each alcohol, there were formed two products, the 3- and the 1-alkoxy nonafluorocyclohexene, the 3-isomers having the lower boiling point and glc retention time in each pair. Following addition to the double bond of

TABLE 1

^{1}H NMR Spectra of 3-Alkoxynonafluorocyclohexenes

Compound Number	Position in Formula					
	$O-CH_2$		CH_2-X		Other	
	δ	Coupling	δ	Coupling	δ	Coupling
B1	4.24	t	3.64	t J_{HH} = 6.0	-	
C1	4.31	t	3.47	t J_{HH} = 6.8	-	
D1	4.26	t	3.26	t J_{HH} = 7.3	-	
E1	4.12	m	3.56	m	OCH_3 3.36	s

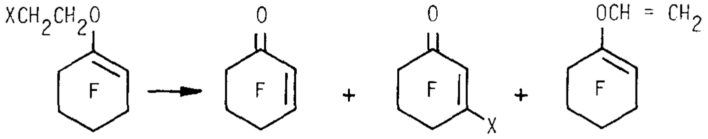
the alkoxide ion, the intermediate anion can decompose in two ways, and the 1-isomers were always the preferred products (1-isomers as % of isolated compounds; 75, B2; 73, C2; 72, D2; 87, E2) as with earlier examples [2,3].

Structures followed simply in each case from spectroscopic parameters:- ir bands were close to 1740 cm^{-1} (CF=CF) or 1705 (CF=COR): ^{19}F nmr peaks for 1-isomers showed 2 sets from CF_2 groups and 1 from vinylic F (intensity ratios 4:4:1) (Table 3); and for 3-isomers intensity ratios of 1:1:1:2:2:2, corresponding to 1 lone F, 2 vinylic F s, and 3 types of CF_2 groups (Table 2).

Pyrolysis Results

Pyrolytic dehydrofluorinations of methyl adducts of decafluorocyclohexene had been studied earlier [4]. Also, the isomeric 2-methoxy- and 6-methoxy-1-methyloctafluorocyclohexenes, on passage over heated nickel at 550°C in an attempt at defluorination/aromatisation, instead underwent pyrolytic demethylation to give 2-methylheptafluorocyclohex-2-enone [2].

Pyrolytic reactions were now studied over packings of hard glass helices, or of fused alumina, in a vertical electrically heated glass tube. The first pyrolysis attempted was of the known [3] 1-(2-acetoxyethoxy)-nonafluorocyclohexene (M; Scheme 2) to try to make the 1-vinyl ether (J).



X = H	G	H		-		-
X = OAc	M	H		-		-
X = OCH_3	E2	H		-		-
X = Br	C2	H	+	K	+	J
X = Cl	B2	H	+	L	+	J
X = OC_6F_9	O	H		-	+	J

Scheme 2

Reaction proceeded smoothly at 510°C over both packings to give essentially one product, which was not however the vinyl ether (J). The same product (H) was formed in good yields by similar pyrolyses of 1-ethoxy- (G) [2] and of 1-(2-methoxyethoxy)- (E2) -nonafluorocyclohexene. At about 400°C, some H was formed but much of the starting materials were recovered.

Compound H analysed as C_6F_8O, its ultraviolet spectrum showed conjugation, and the ^{19}F nmr spectrum supported the structural allocation as octafluorocyclohex-2-enone. This compound (H) has been reported before [5-8] from various other approaches, and the properties correspond. The structure was confirmed by a haloform reaction of enone H using aqueous potassium hydroxide. The preferred mode of haloform cleavage was established. The product (Scheme 3) was 2,2,3,3,4,4,5,6-octafluorohex-5-enoic acid (R), characterised as a salt (R1). The vinylic fluorines had the expected <u>cis</u>-arrangement, and acid R was oxidized to hexafluoroglutaric acid. The direction of the haloform cleavage is as expected. The central C-C bond within the conjugated system is the one broken, the negative charge of the developing carbanion being better accommodated on the original C2, a vinylic FC= group, than on the $-CF_2$ at C6.

TABLE 2

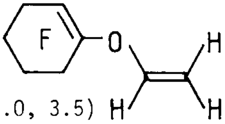
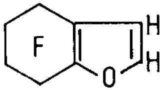
^{19}F NMR Spectra of 3-Alkoxynonafluorocyclohexenes and of Halogenoperfluorocyclohex-2-enones

Compound Number	Position in Formulae									
	6 (CF_2) AB Systems			3 (F-C-OR)	4 or 5 (CF_2)	4 or 5 (CF_2) AB Systems			1 and 2 (CF=CF)	
	δ_A	δ_B	J_{AB}	δ	δ	δ_A	δ_B	J_{AB}	δ	δ
B1	116.3	121.2	290	127.1	130.8	130.8	134.8	268	145.7	155.8
C1	116.5	121.0	282	127.2	130.8	130.8	134.9	274	145.9	155.9
D1	116.6	121.3	284	126.6	129.5	130.9	134.8	275	145.9	156.0
E1	117.0	120.6	282	127.3	131.0	131.0	136.0	272	144.8	157.6
	6 (CF_2)			3 (=CF)	4 (CF_2)	5 (CF_2)			1	2 (=CF)
H	125.5			135.2	119.0	133.2			-	144.1
K	126.0			-	107.9	132.7			-	106.1
L	125.9			-	111.9	132.8			-	116.0

TABLE 3

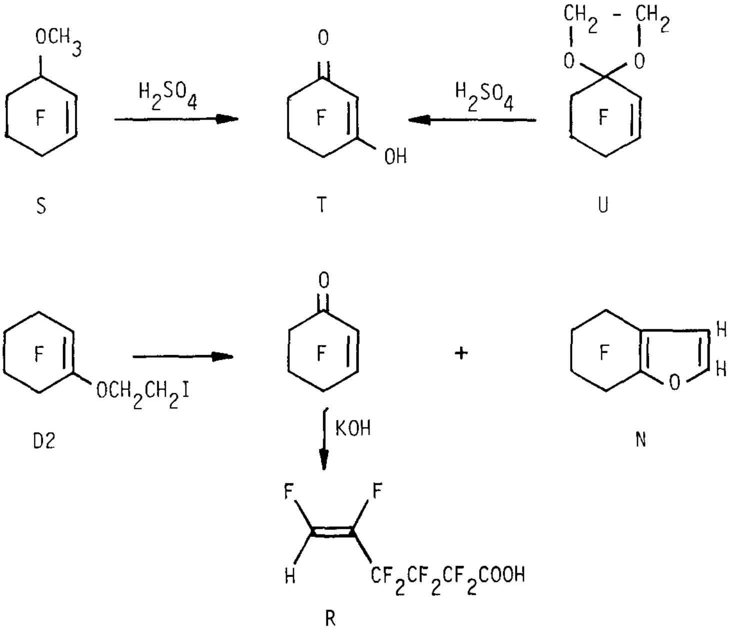
^{19}F and ^{1}H NMR Spectra of 1-Alkoxypolyfluorocyclohexenes

Compound Number	^{19}F NMR Chemical Shifts Position in Formulae			^{1}H NMR Chemical Shifts Position in Formulae					
				$O-CH_2$		CH_2-X		Other	
	3 and 6	4 and 5	2	δ	Coupling	δ	Coupling	δ	Coupling
B2	116.5, 117.1	133.8	156.2	4.55	td $J_{HF} = 2.3$	3.74	t $J_{HH} = 5.8$	-	-
C2	116.6, 117.2	133.9	156.2	4.58	td $J_{HF} = 2.4$	3.54	t $J_{HH} = 6.5$	-	-
D2	116.9	133.9	156.3	4.55	m	3.55	m	-	-
E2	116.8	133.9	156.9	4.40	m	3.60	m	$-OCH_3$ 3.33^3	s
G	117.0	134.1	159.3	3.72	qd $J_{HF} = 3.0$	0.9	td $J_{HH} = 7.0$ $J_{HF} = 0.8$	-	-

J	116.7, 118.0	133.9	149.4		
Intensity Ratios of Peaks	4	4	1		
N	107.0, 111.4	132.9	-		

In earlier work of ours [2], this same structure (H) was put forward for a compound obtained by reaction of sulphuric acid with 3-methoxynonafluorocyclohexene (S; Scheme 3). Demethylations of the same type on saturated methyl perfluorocycloalkyl ethers gave the first syntheses of decafluorocyclohexanone [9] and dodecafluorocycloheptanone [10], and also octafluorocyclopentanone [9]. Clearly, this product (T) of the demethylation of the 3-methoxy-ene (S) could not have had structure H. Compound H had b.p. 72-76^{o}C and was not particularly hygroscopic. Compound T [2] had b.p. 160^{o}C in an anhydrous form, but in moist air readily gave a crystalline trihydrate, m.p. 79-80^{o}C. The respective ir and uv peaks for H and T were disimilar. Nevertheless, compound T was a definite species, since both forms were also obtained [11] by the action of sulphuric acid on a spirodioxalan (U), and had identical characteristics: oxidation of this sample afforded hexafluoroglutaric acid. It seems clear now that compound T must have been 3-hydroxyheptafluorocyclohex-2-enone. By analogy with the reaction [12] of sulphuric acid with decafluorocyclohepta-1,4-diene, the fluorine in position 3 of compounds such as H is susceptible to acidic hydrolysis; it was found also to be replaceable by other halogens (see later) After acidic demethylation of compounds S and U therefore, enone H or a reaction intermediate would suffer hydrolysis of the 3-fluorine to give the keto-enol (T). The first synthesis of compound T had in fact been reported by us earlier [13], from hydrolysis by hydrochloric acid of 1-aminoheptafluorocyclohexen-3-one. The product was very hygroscopic and was isolated as a liquid monohydrate from this aqueous reaction medium; because of the different states of hydration the relationship of the two samples was not realised. Compound T has also been reported since from other reactions [7].

Pyrolysis over glass at 520^{o}C of the 1-(2-bromoethoxide) (C2: Scheme 2) gave three products, the enone H being the major one. The structures of the other two products were established by analytical and spectroscopic data as nonafluorocyclohex-1-enyl vinyl ether (J), and 3-bromononafluorocyclohex-2-enone (K). Pyrolysis at 400^{o}C gave vinyl ether J as the major product, with some H and a little recovered C2, but no bromoenone (K). Pyrolysis over alumina at 520^{o}C gave results similar to those using glass, but, if a second run was carried out immediately following, the proportion of bromoenone K was increased at the expense of H. At 390^{o}C, over alumina, H, J, K and C2 were all present, with J predominant and H the minor constituent.



Scheme 3

Pyrolysis of the 1-(2-chloroethoxide) (B2) over glass at 540°C gave mainly H, and smaller amounts of ether J and of 3-chlorononafluorocyclohex-2-enone (L), the last two being difficult to separate. Over alumina at 520°C, there was rather more J and L formed, but at 400°C little reaction occurred, a trace of H being the only product found.

Formation of the bromoenone K from C2 was favoured over alumina, and this suggested that K and L were each formed from the perfluoroenone H, by exchange of fluorine at position 3 for the other halogen (such 'reverse exchange' processes are known [cf. 14]). Passage of H through the pyrolysis tube, packed with alumina and previously saturated with, respectively, hydrogen bromide and hydrogen chloride, afforded mainly bromoenone K, or chloroenone L, with a little H present in each case. Passage over glass mixed with the appropriate sodium halide gave poorer conversions in both cases. This suggests that these halogen exchanges of enone H and that discussed earlier involving sulphuric acid, could be electrophilic processes, following protonation of the carbonyl group. Loss of fluorine could be preferred because the halide or sulphate groups take up equatorial positions after addition, the fluorine then being lost from the stereochemically-preferred axial position [cf. 15].

The detailed structures of the enones K and L followed from their ^{19}F nmr spectra. Consideration of published data for decafluorocyclohexene [16] and for 1-chloro- and 1-bromo-nonafluorocyclohexene [17] shows differences in the chemical shifts of, respectively, -30.0 and -39.2 for vinylic fluorines, and -6.9 and -10.8 for CF_2, adjacent to the non-fluorine substituent, with no significant difference in more distant positions. It will be seen from Table 2 that the differences for enones L and K relative to H are:- position 2: L, -28.1; K, -38.0: position 4: L, -7.9; K, -11.1. Further, for the known [7] isomeric 2-chlorononafluorocyclohex-2-enone, the only significant change in ^{19}F chemical shift values, relative to those of compound H, is at position 3 (-29.8).

The iodo-ether (D2) was less stable to heat than the other ethers studied, and decomposed completely over glass at 395^{o}C. The products were enone H and a new heterocycle (N) (ratio ca. 2:1) (Scheme 3) and, surprisingly, no vinyl ether J was found. Analysis and spectroscopy showed that compound N was 6,6,7,7,8,8,9,9-octafluoro-2-oxabicyclo[4,3,0]nona-1(5), 3-diene. As expected, bis-1,2-(nonafluorocyclohex-1-enoxy)ethane [3] was pyrolysed to give only enone (H) and vinyl ether (J).

Three of the 3-substituted ethers were pyrolysed also. All decomposed more readily than their 1-isomers. The 3-(2-methoxyethoxide) (E1) decomposed completely at 395^{o}C over alumina to give exclusively enone H and no ethers were detected. Similar conditions with the isomer E2 had given H and recovered E2 in a ratio 1:2.

The 3-(2-bromoethoxide) (C1) over alumina at 400^{o}C gave enone H, recovered C1, and its isomer C2. Though an inseparable mixed fraction was also obtained, the amounts of J and K produced must have been much less than from the comparable reaction using isomer C2.

3-Ethoxynonafluorocyclohexene (Q) decomposed largely at 395^{o}C, the product being mainly H, but with a little recovered Q and a roughly equal amount of its 1-isomer (G). Hence, the readier pyrolytic decomposition of the 3-alkoxy-isomers is accompanied by isomerisation of them to the more stable 1-alkoxy-isomers. A similar effect was observed before, in the cases of the pair of methyl-methoxy-compounds already mentioned [2]. From the proportions of the products however, the 3-alkoxy-isomers must decompose to enone H themselves, and not entirely via rearrangement to the 1-isomers; decomposition and isomerisation must proceed concomitantly. No isomerisatio of 1-alkoxides to 3-isomers was detected.

Pyrolysis of alkoxy derivatives offers a good synthetic route to polyfluoroenones in some cases. Decafluorocyclohept-2-enone was made [18] by pyrolysis of 1-ethoxyundecafluorocycloheptene, and octafluorocyclohepta-2,4-dienone from 1-ethoxynonafluorocyclohepta-1,3-diene. 1- and 3-ethoxynonafluorocyclohexenes (G and Q) are readily made, and pyrolysis of the mixture affords a good route to octafluorocyclohex-2-enone (H).

These pyrolyses of alkoxy-nonafluorocyclohexenes could well proceed via the usual types of cyclic transition states [19], postulated for example [20], in the pyrolyses of pentafluorophenetole and its derivatives to give pentafluorophenol. Processes of this sort would give keto or enol intermediates (e.g. analogous to A or B of ref. 18). An alternative hypothesis would involve heterolytic reactions on the packing surface; firstly, heterolytic fission of the alkyl-oxygen bond to give a nonafluorocyclohexenyl- -1-oxy (from 1-isomers) or -3-oxy (from 3-isomers), anion, which would then lose fluoride ion, from the 3 position in both cases, to give enone H. Whatever the detailed pathway, it is of interest that this C-O bond breaks in all cases, sometimes exclusively, and that this occurs in preference to loss of acetoxy (compound M). It did not seem that the vinyl ether J broke down rapidly once formed, and in the cases of the chloro- and bromo-ethers (B2 and C2), two processes occurred together; cleavage of the C-O bond as above to give enone H, and of the C-Cl or C-Br bond to give vinyl ether J. With the iodo-ether (D2) the preferential bond breakage, even at the lower temperatures used, was still the C-O bond as above but the C-I bond also broke, presumably homolytically, (there was a large peak in the mass spectrum from loss of iodine), and the intermediate cyclised to give eventually the benzofuran N.

EXPERIMENTAL

Techniques

These were as reported before [3]. A further glc column was used: unit 7, silicone gum on Chromosorb P 30-60 mesh (1:6) (910 x 0.6 cm).

Spectroscopic measurements were taken as before. Nmr results are given in Tables 1-3 (s = singlet, d = doublet, t = triplet, AB = AB quartet, q = quartet, m = multiplet).

Preparation of Alkoxy-nonafluorocyclohexenes

General Method The substituted ethanol was added dropwise to a stirred suspension of sodium hydride in decafluorocyclohexene (A) and the mixture stirred for 1 hour. Water (70 cm^3) was then added cautiously, and the lower layer separated, washed with water (2 x 30 cm^3), dilute hydrochloric acid (20 cm^3; 4M), dried and distilled.

From 2-chloroethanol (17.0 g), NaH (5.0 g) and C_6F_{10} (30.0 g) the product (34.5 g) afforded by distillation: (i), recovered C_6F_{10} (3.0 g) (glc and ir): (ii), a colourless liquid (27.7 g) b.p. 40-60°C/0.2 mm Hg. Part of fraction (ii) (3.0 g) was separated by glc (1, 127°C, 5.6) to give:- (ii)a, 3-(2-chloroethoxy)nonafluorocyclohexene (B1) nc (0.57 g), b.p. 167°C (Found: C, 29.7; H, 1.5. $C_8H_4ClF_9O$ requires C, 29.8; H, 1.25%); m/e 266 ($C_5{}^{35}ClF_9$); ir 1740 cm^{-1} (s; CF=CF): (ii)b, 1-(2-chloroethoxy)nonafluorocyclohexene (B2) nc (1.71 g), b.p. 171°C (Found: C, 29.4; H, 1.0%); m/e 324, 322 (M); ir 1705 (s; C=C). Products made by reaction of PCl_5 with hydroxyethers were identical [21].

2-Bromoethanol (32.0 g), NaH (5.6 g) and C_6F_{10} (30.0 g) gave product (36.0 g) separated by distillation into: (i), C_6F_{10} (4.2 g): (ii), a colourless liquid (26.2 g), b.p. 40-70°C/0.1 mm Hg. Glc (1, 127°C, 5.6) on fraction (ii) (3.0 g) gave: (ii)a, 3-(2-bromoethoxy)nonafluorocyclohexene (C1) nc (0.59 g), b.p. 179°C (Found: C, 26.4; H, 1.0. $C_8H_4BrF_9O$ requires C, 26.2; H, 1.1%); m/e 368, 366 (M); ir 1740 cm^{-1}: (ii)b, 1-(2-bromoethoxy)nonafluorocyclohexene (C2) nc (1.60 g), b.p. 185°C (Found: C, 26.1; H, 1.4; Br, 22.2; F, 46.7%); m/e 368, 366; ir 1705 cm^{-1}.

Distillation of the product (29.6 g) from 2-iodoethanol (44.0 g), NaH (5.6 g) and C_6F_{10} (30.0 g) afforded:- (i), C_6F_{10} (18.0 g): (ii), a pink liquid (6.9 g) b.p. 50-72°C/0.2 mm Hg. The latter (1.12 g) was separated by glc (7, 120°C, 2.5) into: (ii)a, 3-(2-iodoethoxy)nonafluorocyclohexene (D1) nc (0.20 g) (Found: C, 23.3; H, 0.8. $C_8H_4F_9IO$ requires C, 23.2; H, 1.0%); m/e 414 (M), 287 (M-I); ir 1740 cm^{-1}: (ii)b, a mixture (0.05 g) of (ii)a and (ii)c: (ii)c, 1-(2-iodoethoxy)nonafluorocyclohexene (D2) nc (0.52 g) (Found: C, 23.1; H, 1.0%); ir 1705 cm^{-1}.

2-Methoxyethanol (10.0 g), NaH (3.0 g) and C_6F_{10} (30.0 g) gave a product (32.4 g) separated by distillation into:- (i), C_6F_{10} (0.5 g): (ii), a colourless liquid (23.0 g) b.p. 40-60°C/0.2 mm Hg: (iii), a yellow viscous liquid (6.2 g) b.p. 60-110°C/0.2 mm Hg, not containing the major products. Fraction (ii), by glc (5, 80°C, 12) afforded: (ii)a, 3-(2-methoxyethoxy)nonafluorocyclohexene (E1) nc (0.5 g), b.p. 167°C (Found: C, 34.1; H, 2.4; F, 53.9. $C_9H_7F_9O_2$ requires C, 34.0; H, 2.2; F, 53.7%); m/e 298 (M-HF); ir 1740 cm^{-1}: (ii)b, 1-(2-methoxyethoxy)nonafluorocyclohexene (E2) nc (3.2 g), b.p. 171°C (Found: C, 33.8; H, 2.5; F, 53.9%); m/e 318 (M); ir 1705 cm^{-1}.

Pyrolyses of Alkoxy-nonafluorocyclohexenes

General Method

A vertical Pyrex glass tube (36 cm x 2.4 cm int. diam.) supported in an electric furnace (heated section 30 cm) was used. Temper atures (range 290-550°C) were measured by a thermocouple. The tube was packed with either silica-borate glass single turn helices (Gallenkamp) (Packing P1) or fused alumina anti-bumping granules (B.D.H.) (Packing P2), supported on a plug of glass wool. Nitrogen (British Oxygen Co., white spot grade) was passed through the tube at 0.8 l h^{-1} (controlled by a flowmeter) whilst the sample was introduced at *ca*. 0.2 g min^{-1} by means of a pressure-equalised dropping funnel. The pyrolysate was collected at the bottom of the tube in a glass trap cooled by liquid air, and after each addition nitrogen was passed at 1 l h^{-1} for 5 hours further at the same temperature. When the packing was changed, the tube at 550°C was purged with nitrogen (*ca*. 1 l h^{-1}) for 72 hours.

1-Ethoxynonafluorocyclohexene (G)

Pyrolysis (510°C; Packing P1) of G (1.84 g) [2] gave a product (1.56 g) with only 1 component shown by glc. Distillation from P_2O_5 afforded octafluorocyclohex-2-enone (H) (1.2 g) b.p. 72-76°C (Found: *M* 239.983. Calc. for C_6F_8O: *M* 239.982); ir 1750 (s) 1695 (s); λ_{max} 223 (ϵ 11,600 in cyclohexane); reported previously [5-8].

G (1.62 g; 390°C; Packing P1) gave pyrolysate (1.41 g), separation of 0.51 g of which by glc (1, 90°C, 5.6) afforded H (0.09 g) and G (0.34 g). Similar experiments over Packing P2 gave analogous products in each case in slightly lower recoveries.

1-(2-Bromoethoxy)nonafluorocyclohexene (C2)

At 520°C (Packing P1), C2 (0.47 g) afforded product (0.30 g) separated by glc (1, 130°C, 10: 0.11 g passed) into: (i), enone H (0.4 g): (ii), nonafluorocyclohex-1-enyl vinyl ether (J) nc (0.02 g), b.p. 103°C (Found: C, 33.6; H, 1.1; F, 59.5. $C_8H_3F_9O$ requires C, 33.6; H, 1.1; F, 59.8%); m/e 286 (M); ir 1710 (s) 1650 (s): (iii), 3-bromoheptafluorocyclohex-2-enone (K) nc (0.01 g) (Found: M, 299.902. $C_6{}^{79}BrF_7O$ requires M 299.902); m/e 302 ($C_6{}^{81}BrF_7O$); ir 1745 (s), 1630 (s). Analytical glc showed, besides peaks due to these products, three minor peaks due to components which could not be isolated.

At 400°C (Packing P1), C2 (1.03 g) afforded products (0.92 g); glc (0.34 g) gave H (0.07 g); J (0.13 g) and recovered C2 (0.06 g), no K being detected.

Over packing P2, results at 520°C were comparable to those with P1: from a second run immediately afterwards, the proportion of K increased at the expense of H. At 390°C, products were (% by weight of C2 used): H, 4; J, 22; K, 11; C2, 13.

1-(2-Chloroethoxy)nonafluorocyclohexene (B2)

Over packing P1 at 540°C, compound B2 (1.59 g) gave a product containi 3 major and 6 minor components. Glc separation (7, 70°C, 2.4: 0.64 g) yielded: (i), enone H (0.23 g): (ii), a mixture (0.05 g), mainly vinyl ether J, + a little L: (iii), 3-chloroheptafluorocyclohex-2-enone (L) nc (0.07 g) (Found: M, 255.955. $C_6{}^{35}ClF_7O$ requires M 255.953); m/e 258 ($C_6{}^{37}ClF_7O$); ir 1755 (s), 1645 (s).

Over packing P2 at 520°C, yields of H were as above, and of J and L slightly higher; a trace of B2 was recovered. At 400°C, B2 (65%) was recovered, the only product being a trace of H.

1-(2-Acetoxyethoxy)nonafluorocyclohexene (M)

Compound M [3] (0.88 g) pyrolysed at 510°C over packing P1 gave a product (0.68 g) showing only the major peak (>95%) by glc. Separation by glc (1, 90°C, 5.6: 0.38 g) gave enone H (0.25 g).

A similar experiment over packing P2 (540°C) gave a slightly poorer yield of H. Over P2 at 290°C, 36% of starting material M was recovered, and 15% by weight of enone H was the only product isolated.

1-(2-Methoxyethoxy)nonafluorocyclohexene (E2)

Over packing P1 at 520°C, compound E2 (1.09 g) gave pyrolysate (0.84 g) containing one major and six very minor components. Glc (1, 90°C, 4.3: 0.42 g) gave enone H (0.22 g). At 390°C, H (28%) and C2 (35%) were obtained. Over packing P2, at 540°C, H (48%) was obtained: at 390°C, H (21%) and C2 (44%; all percentages are by weight of C2 used): at 290°C no reaction was detected.

1-(2-Iodoethoxy)nonafluorocyclohexene (D2)

Over packing P1 at 395°C, compound D2 (1.25 g) afforded a product (1.07 g) essentially containing iodine and two organic components. Glc (7, 100°C, 4.9: 0.37 g) gave: (i), enone H (0.16 g): (ii), 6,6,7,7,8,8,9,9-octafluoro-2-oxabicyclo[4,3,0]nona-1(5),3-diene (N) nc (0.07 g) (Found: C, 36.3; H, 0.9%; *M*, 265.995. $C_8H_2F_8O$ requires C, 36.1; H, 0.8%; *M*, 265.998); ir 1640, shoulder 1625 (m).

Bis-1,2-(nonafluorocyclohex-1-enoxy)ethane (O)

Compound O [3] (0.41 g) was pyrolysed over packing P2 at 530°C, and the product (0.31 g) separated by glc (1, 90°C, 10.0: 0.10 g) to give: (i), enone H (0.05 g): (ii), vinyl ether J (0.007 g).

3-Ethoxynonafluorocyclohexene (Q)

Compound Q [2] (0.25 g) pyrolysed over packing P2 at 395°C afforded a mixture (0.20 g); separation by glc (2, 90°C, 3.5: 0.092 g) gave: (i), enone H (0.039 g): (ii), 3-ethoxy-ene (Q) (0.005 g): (iii), 1-ethoxy-ene (G) (0.006 g).

3-(2-Bromoethoxy)nonafluorocyclohexene (C1)

Compound C1 (0.79 g) at 400°C over packing P2 gave a complex mixture (0.64 g) separation of part of which by glc (1, 83°C-120°C, 5.6: 0.40 g) yielded: (i), enone H (0.068 g): (ii), a mixture of at least five components (0.031 g): (iii), the 3-(2-bromoethoxy)ene (C1) (0.102 g): (iv), the 1-(2-bromoethoxy)ene (C2) (0.045 g).

3-(2-Methoxyethoxy)nonafluorocyclohexene (E1)

Compound E1 (0.79 g) over packing P2 at 395° gave pyrolysate (0.27 g) shown to be largely (*ca*. 95%) enone H. A pure specimen was isolated (glc as before).

Reactions of Octafluorocyclohex-2-eneone (H)

With Hydrogen Chloride The pyrolysis tube at 545°C (Packing P2) was saturated with hydrogen chloride gas and enone H (2.02 g) passed through over 40 minutes. The product (1.43 g) was separated by glc (7, 90°C, 1.9; 0.9 g passed) to give: (i), enone H (0.10 g); (ii), 3-chloro-enone L (0.63 g).

With Hydrogen Bromide An analogous reaction to I afforded product (2.13 g); separation of 1.64 g (7, 100°C, 4.9) giving: (i), enone H (0.18 g) (ii), 3-bromo-enone K (1.07 g).

With Sodium Chloride The pyrolysis tube was at 520°C and contained a mixture of packing P1 and powdered sodium chloride (3:8). Enone H (1.71 g) gave product (1.47 g), of which 1.12 g (7, 100°C, 3.5) gave H (0.53 g) and L (0.18 g).

With Sodium Bromide In an analogous way at 540°C, H (1.44 g) gave product (1.12 g) of which 0.84 g (1, 100°C, 4.3) was separated into H (0.38 g) and K (0.17 g).

With Aqueous Potassium Hydroxide Potassium hydroxide solution (4M; 35 cm^3) was added to enone H (5.5 g) and the mixture shaken at 15°C for 20 min. Unreacted H (0.5 g) remained undissolved. The aqueous layer was poured into ice-water (100 cm^3) acidified with sulphuric acid (4M) and extracted with ether (4 x 40 cm^3). Drying followed by evaporation left a syrupy residue (5.7 g) of crude Z-2,2,3,3,4,4,5,6-octafluorohex-5-enoic acid (R). ^1H nmr; δ 12.71 (s, $-CO_2H$), 9.15 (dd, J_{HF} = 72.7, J_{HF} = 14.5, $=C\genfrac{}{}{0pt}{}{\diagup H}{\diagdown F}$), intensity ratio 1:1. ^{19}F nmr; 119.1 (m), 124.3 (m), 155.3 (m, -CF=C), 154.7 (dd, J_{HF} = 72.7, $J_{FF\underline{cis}}$ = 6.0, $=C\genfrac{}{}{0pt}{}{\diagup H}{\diagdown F}$), intensity ratio 2:4:1:1.

To an aliquot (1.4 g) of R in water (20 cm^3) was added a saturated solution in water of S-benzylthiouronium chloride to give a precipitate (1.5 g). Recrystallisation of part (0.6 g) from water afforded the S-benzylthiouronium salt (R1) nc (0.4 g), m.p. 157-159°C (Found: C, 39.6; H, 2.9; F, 35.6; N, 6.8. $C_{14}H_{12}F_8N_2O_2S$ requires C, 39.6; H, 2.9; F, 35.8; N, 6.6%). A further aliquot (1.5 g) of crude acid R was oxidised by potassium permanganate in acetone in the usual way [cf. 1] to give dianilinium hexafluoroglutarate (1.0 g) [1].

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