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POLYFLUORO-COMPOUNDS BASED ON THE CYCLOHEPTANE RING SYSTEM. PART 7. ETHOXYPOLYFLUOROCYCLOHEPTENES AND POLYFLUOROCYCLOHEPTENONES

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SUMMARY

Dodecafluorocycloheptene and ethanolic potassium hydroxide afforded 1-ethoxyundecafluorocycloheptene which at 410°C decomposed to decafluorocyclohept-2-enone. Decafluorohepta-1,3-diene likewise gave mainly 1-ethoxynonafluoro-, together with some 1,4-diethoxyoctafluoro-cyclohepta-1,3-diene. The 1-ethoxy-1,3-diene was photoisomerised to 1-ethoxynonafluorobicyclo-(3,2,0)hept-6-ene (proving its structure), and was decomposed on pyrolysis at 430°C to give a complex mixture, from which octafluorocyclohepta-2,4-dienone was isolated.

INTRODUCTION

Extending the range of compounds made from polyfluorocycloheptanes [1], this investigation led to the synthesis of two new derivatives related to hexafluorotropone, the first preparation of which we have reported earlier [2]. The approach used started from alkoxy-derivatives of perfluorocycloheptenes. It has been found [3] that heating 1-methoxy- and 6-methoxy-2-methyloctafluorocyclohexene afforded 1-methylheptafluorocyclohex-1-ene-6-one; subsequently [4], octafluorocyclohex-2-enone was made by pyrolysis of several 1-alkoxynonafluorocyclohexenes, the 1-ethoxy-derivative giving a good yield of the enone. This paper records the preparation from dodecafluorocycloheptene (I; See Scheme) [5], and decafluorocyclohepta-1,3-diene (II) [6], of their 1-ethoxy-derivatives, followed by pyrolysis of the latter to perfluorocycloheptenones.

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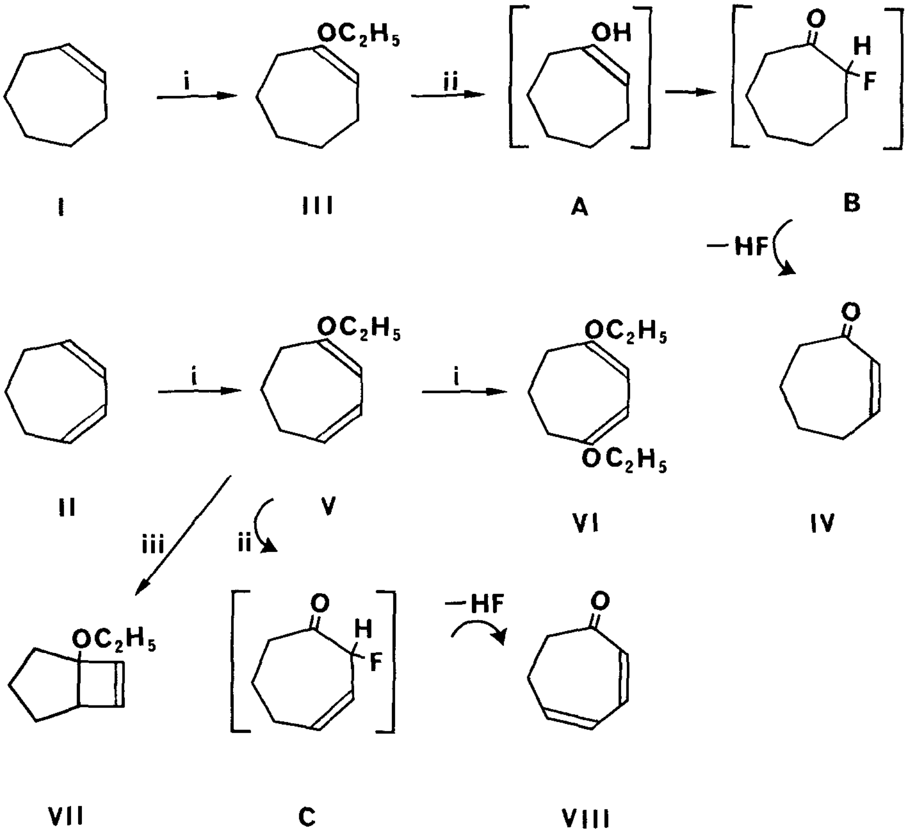

Reactions: i, C_2H_5OH/KOH; ii, heat (ca. 420°C); iii, uv light.

All unmarked bonds are to FLUORINE

Scheme

RESULTS AND DISCUSSION

Dodecafluorocycloheptene (I) had previously been treated with methanol in the presence of potassium hydroxide, and had given [5] mainly 1-methoxyundecafluorocycloheptene, with some of the isomeric 3-methoxide (5.7 : 1), and also some 1,2-dimethoxydecafluorocycloheptene. In the homologous decafluorocyclohexene series, the proportion of the 3-alkoxy-isomer was smaller with ethanol than with methanol [3]. Further, dodecafluorocycloheptene generally gives 1-substituted cycloheptenes on nucleophilic attack [7]. It was expected therefore that ethoxylation of cycloheptene I would give largely the 1-ethoxide.

Compound I was treated with ethanol and potassium hydroxide under the conditions used for similar reactions [3], and, in fact, besides unreacted I, only one product was detected. This was clearly 1-ethoxy-undecafluorocycloheptene (III) from the analysis and nmr spectra (see Table). There was only one peak for vinylic fluorine, but five due to $>CF_2$ groups, including two at slightly lower field, from the positions on either side of the double bond. Decomposition of ethoxide III proceeded smoothly at 410°C, on passage through a tube packed with glass helices. The product analysed as $C_7F_{10}O$. It had two infrared bands due to unsaturation, and selective absorption in the ultraviolet typical of a conjugated structure. Oxidation afforded octafluoroadipic acid. The ^{19}F nmr spectrum confirmed that the compound was decafluorocyclohept-2-enone (IV); four peaks due to $>CF_2$, and two to vinylic F were found.

The likeliest reaction pathway for this pyrolysis is loss of ethylene from the ethoxy group, followed subsequently by loss of HF (detected in the cold trap). Whether intermediates such as A or B, shown in the Scheme, have real existence is open to conjecture. One or both could be distinct stages in the process, or the entire decomposition could be simultaneous.

The major products from reactions under basic conditions of methanol [8] and ethanol [9] with octafluorocyclohexa-1,3-diene were 2-alkoxy-1,3-dienes. However, following the reaction of decafluorocyclohepta-1,3-diene (II) with sodium borohydride [2], it was expected that this diene and ethanolic potash would give a 1-ethoxylated derivative. Such was the case: the product was a multi-component mixture, but with two major constituents (V and VI; ratio 7:1, respectively). The larger (V) analysed as an ethoxynonafluorocycloheptadiene, and was conjugated, though ^{19}F nmr could not distinguish between the 1- and 2-ethoxy structures. This was done by photoisomerisation with ultraviolet light, a reaction already wellestablished for polyfluorocyclohepta-1,3-dienes [10, 1]. The product (VII), isomeric with compound V, had a ^{19}F nmr spectrum showing two vinylic fluorines and only one in a tertiary (bridgehead) position, besides three $>CF_2$ groups. Clearly, therefore the structure was 1-ethoxynonafluorobicyclo(3,2,0)hept-6-ene (VII), and its precursor (V) was 1-ethoxynonafluorocyclohepta-1,3-diene. The other product of the ethoxylation, (VI), was a di-ethoxide and was conjugated. It had clearly a symmetrical structure based on the simplicity of its ^{19}F and ^{1}H nmr spectra, and was 1,4-diethoxy-octafluorocyclohepta-1,3-diene (VI).

Pyrolysis of the 1-ethoxy-diene (V) proceeded smoothly at 430°C, but gave a very complex mixture, showing at least 15 peaks on glc. Fortunately, one major peak was present and the compound concerned (VIII) was isolated successfully in small quantity, together with a little of the bicyclo-ene (VII). Product VIII analysed as C_7F_8O and its uv spectrum showed conjugated unsaturation. The ir spectrum had three bands in the region 1650-1730 cm^{-1}. There were four different absorptions due to vinylic fluorines in the ^{19}F nmr spectrum, and one peak arising from both $>CF_2$ groups. Thus, compound VIII was octafluorocyclohept-2,4-dieneone. Again, some HF was present in the crude pyrolysis product, and an intermediate such as C in the Scheme is a possible stage in the decomposition pathway. A major peak in the mass spectrum of the ethoxy-diene (V) corresponded to loss of C_2H_4.

Neither the decafluoro-eneone (IV) nor the octafluorodieneone (VII) showed any great tendency to form a hydrate (normal isolation techniques were adequate). Most perfluoroketones with saturated perfluoroalkyl groups form hydrates very readily.

EXPERIMENTAL

General

Spectroscopic parameters were measured as described earlier [2]. Gas liquid chromatography was done on semi-preparative glass columns (9 m x 10 mm) in a Pye 104 unit : column A, dinonyl phthalate/Celite (1:2); column B, polyethylene glycol adipate/Chromosorb P (1:6); column C, silicone gum (Si 301)/Celite (1:6). Also used was a preparative column D, 4.8 m x 75 mm packed with silicone gum (Si 301)/Celite (1:5). Given for each separation are the column used, temperature (°C) and nitrogen flow rate ($l\ h^{-1}$).

TABLE

Nmr Spectra of New Compounds

Compound Number		Chemical Shift	Relative Intensity	Position in Formula	Type of Signal and Couplings
III	F	113.4	2	3,7	c
		114.3	2		c
		127.9	2	4,5,6	c
		128.9	2		c
		129.6	2		c
		141.4	1	2	p
	H	1.40	3	CH_3	t, J = 6.5
		4.22	2	CH_2	q, J = 6.5
IV	F	114.4	1	4,7	c
		118.6	1		c
(in $CDCl_3$)		127.6	1	5,6	c
		128.5	1		c
		136.3	1	2,3	c, 2 separate signals
V	F	119.0	2	5,7	c
		120.5	2		c
		128.5	2	6	p
		141.0	1	2,3	c
		145.2	1		cdt
		153.1	1	4	dt, J_d = 21.7, J_t = 6.5
	H	1.40	3	CH_3	t, J = 7
		4.30	2	CH_2	dq, J_q = 7, J_d = 2
VI	F	117.5	2	5,7	p, J = 5.6
		127.0	1	6	p, J = 5.6
		138.8	1	2,3	c
	H	1.30	3	CH_3	t, J = 7
		4.10	2	CH_2	q, J = 7
VII	F	113.5	1	7	d, J = 14
		123.3	1	6	t
		118.6, 142.6	2	2,3,4	AB, J = 255
		120.8, 129.7	2		AB, J = 255
		122.7, 133.3	2		AB, J = 255
		193.4	1	5	c
	H	1.35	3	CH_3	t, J = 7.5
		3.90	2	CH_2	q, J = 7.5
VIII	F	123.1	4	6,7	c
		130.4	1	2	c
		141.1	1	3,4,5	c
		143.9	1		c
		145.7	1		c

c = complex, d = doublet, t = triplet, q = quartet, p = pentet , AB = AB quartet.

Reaction of dodecafluorocycloheptene (I) with ethanolic potassium hydroxide

Dry ethanol (4.4 cm^3) was added dropwise to a stirred mixture of dodecafluorocycloheptene (I) (18 g) and powdered potassium hydroxide (3.8 g) at 15°C, so that slight heat of reaction developed. Potassium fluoride was precipitated. After completion of the addition, stirring was continued for 1 h, and then water (70 cm^3) was added. The lower layer was separated, washed with water (2 x 50 cm^3), and distilled from P_2O_5. Analytical glc on the product (17.0 g) showed 2 components only. Separation by glc (D, 80°, 50) gave: (i) recovered dodecafluorocycloheptene (I) (1.8 g) (glc and ir); (ii) 1-ethoxyundecafluorocycloheptene (III) nc (10.2 g) b.p. 142-143°C (Found: C, 32.1; H, 1.6; F, 61.7. $C_9H_5F_{11}O$ requires C, 32.0; H, 1.5; F, 61.8%); M/e 338 (M); ir 3000-2900 (m), 1735 (s).

Pyrolysis of 1-ethoxyundecafluorocycloheptene (III)

The reaction was done in a Pyrex glass tube, (300 mm x 2 mm diam.), packed with single-turn glass helices, and heated to 410°C; compound III (1.6 g) was passed through during 20 min., in a stream of nitrogen (0.9 $l\ h^{-1}$). The product was trapped by liquid nitrogen and, on being warmed, evolved hydrogen fluoride to leave a liquid (1.4 g). After distillation in vacuo from P_2O_5, glc separation (A, 90°, 4; 1.1 g passed) afforded: (i) decafluorocyclohept-2-enone (IV) nc (0.8 g), b.p. 86-87°C (Found: C, 28.9; F, 65.3. $C_7F_{10}O$ requires C, 29.0; F, 65.5%); M/e 290 (M); ir 1750, (m), 1685 (m); λ_{max} 236 nm (ε, 6060 in cyclohexane); (ii) recovered starting material (III) (0.05 g) (glc and ir).

Oxidation of the enone (IV)

Compound IV (0.5 g), potassium permanganate (0.6 g) and dry acetone (50 cm^3) were stirred together at 15°C for 12 hours. Water (50 cm^3) was added and the acetone removed by rotary evaporation under reduced pressure. The solution was acidified (4 M H_2SO_4), decolourised with SO_2, and extracted continuously with ether for 24 hours. The ether solution was dried ($MgSO_4$) concentrated (to 10 cm^3) and aniline added to give dianilinium octafluoroadipate (0.6 g) m.p. 210-211°C [*cf.* 3], with a correct nmr spectrum.

Reaction of decafluorocyclohepta-1,3-diene (II) with ethanolic potassium hydroxide

Dry ethanol (4.0 cm^3) was added dropwise to a stirred mixture of diene II (15.0 g) and powdered potassium hydroxide (3.9 g), as for olefin I. After the water wash, the product was dried ($MgSO_4$). The mixture (15.1 g) on analytical glc showed one major and two minor peaks besides a little starting material. Separation by glc (C, 140°, 3.6; 1.4 g passed) gave: (i) starting material (II) (0.06 g) (glc and ir); (ii) a mixture (1.0 g); (iii) a trace component; (iv) 1,4-diethoxyoctafluorocyclohepta-1,3-diene (VI) nc (0.11 g), b.p. 172-173°C (Found: C, 40.2; H, 3.6; F, 47.0. $C_{11}H_{10}F_8O_2$ requires C, 40.5; H, 3.1; F, 46.6%); M/e 326 (M); ir 3000-2900 (m), 1675 (s); λ_{max} 265 nm (ε, 6800 in ethanol); (v) a trace component. Fraction (ii) was re-separated by glc (A, 100° 6.5) to give: (iia) a mixture (0.05 g) not investigated further; (iib) 1-ethoxynonafluorocyclohepta-1,3-diene (V) nc (0.78 g), b.p. 147-148°C (Found: C, 35.8; H, 1.9; F, 57.5. $C_9H_5F_9O$ requires C, 36.0; H, 1.7; F, 57.0%); M/e 300 (M), 272 (s; $M-C_2H_4$); ir 3000-2900 (m), 1715 (m), 1680 (s); λ_{max} 257 nm (ε, 6830 in ethanol).

Photoisomerisation of 1-ethoxynonafluorocyclohepta-1,3-diene (V)

Compound V (2.0 g) was sealed in a quartz tube, and irradiated by uv light (Hanovia medium pressure lamp) for 6 days. Distillation afforded 1-ethoxynonafluorobicyclo-(3,2,0)-hept-6-ene (VII) nc (1.85 g), b.p. 123°C (Found: C, 36.2; H, 1.9; F, 56.6%); M/e 300 (M); ir 3000-2900 (m), 1780 (s).

Pyrolysis of 1-ethoxynonafluorocyclohepta-1,3-diene (V)

Pyrolysis as before but at 430°C of the diene (V) (1.6 g) gave, after loss of some HF, a yellow liquid (1.28 g), which by analytical glc showed at least 15 peaks. This product (11.2 g) was distilled under reduced pressure through a vacuum-jacketted column (80 mm long, packed with glass helices) and the fraction (4.0 g), containing the major component, was collected. Separation by glc (B, 70°, 5) gave: (i) a mixture (0.5 g); (ii) 1-ethoxynonafluorobicyclo(3,2,0)hept-6-ene (VII) (0.25 g) (glc and ir); (iii) octafluorocyclohepta-2,4-dienone (VIII) nc (1.8 g), b.p. 125°C (Found: C, 33.4; F, 60.9. C_7F_8O requires C, 33.35; F, 60.3%); M/e 252 (M); ir 1730, shoulder 1710 (s), 1650 (m); λ_{max} 301 nm (ε, 5800 in cyclohexane).

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