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POLYFLUORO-1,2-EPOXY -ALKANES AND -CYCLOALKANES. PART V. SOME POLYFLUORO-1,2-EPOXIDES IN THE CYCLOHEPTANE SERIES

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SUMMARY

Dodecafluorocycloheptene and 4,5-dibromodecafluorocycloheptene (made from the 1,4-diene) gave the corresponding 1,2-epoxides with aqueous sodium hypochlorite/acetonitrile. The epoxy-ring of dodecafluoro-1,2-epoxycycloheptane was opened by, (i) sodium methoxide, the product being further methylated with dimethyl sulphate to give 1,1,2-trimethoxyundecafluorocycloheptane; (ii) potassium fluoride, giving an alkoxide which on being heated decomposed to dodecafluorocycloheptanone. Decafluorocyclohepta-1,4-diene was oxygenated by aqueous sodium hypobromite/acetonitrile to give decafluoro-(1,2)(4,5)-diepoxycycloheptane. The 1,3-diene analogously afforded decafluoro-1,2-epoxycyclohept-3-ene and decafluoro-6,7-epoxy-8-oxabicyclo(3,2,1)octane: the former and potassium fluoride gave decafluorocyclohept-2-enone, whilst the latter with lithium aluminium hydride afforded 6H,7H-nonafluoro-8-oxabicyclo(3,2,1)octa-6-ol. Pyrolysis of dodecafluoro-1,2-epoxycycloheptane at 500°C over a packing of hard glass afforded decafluorocyclohept-2-enone and hexafluorobenzene. Decafluoro-1,2-epoxycyclohexane under similar conditions gave octafluorocyclohex-2-enone and octafluorocyclopentene, whilst decafluorocyclohexanone gave octafluorocyclohex-2-enone.

INTRODUCTION

Results described already in this Series include the pyrolyses [1] of epoxides made [2] from oligomers of tetrafluoroethene, and syntheses [3] and oxygen-ring-opening reactions [4] of epoxides derived from polyfluorocyclohexenes. This paper reports the first syntheses and reactions of epoxides in the polyfluorocycloheptane series.

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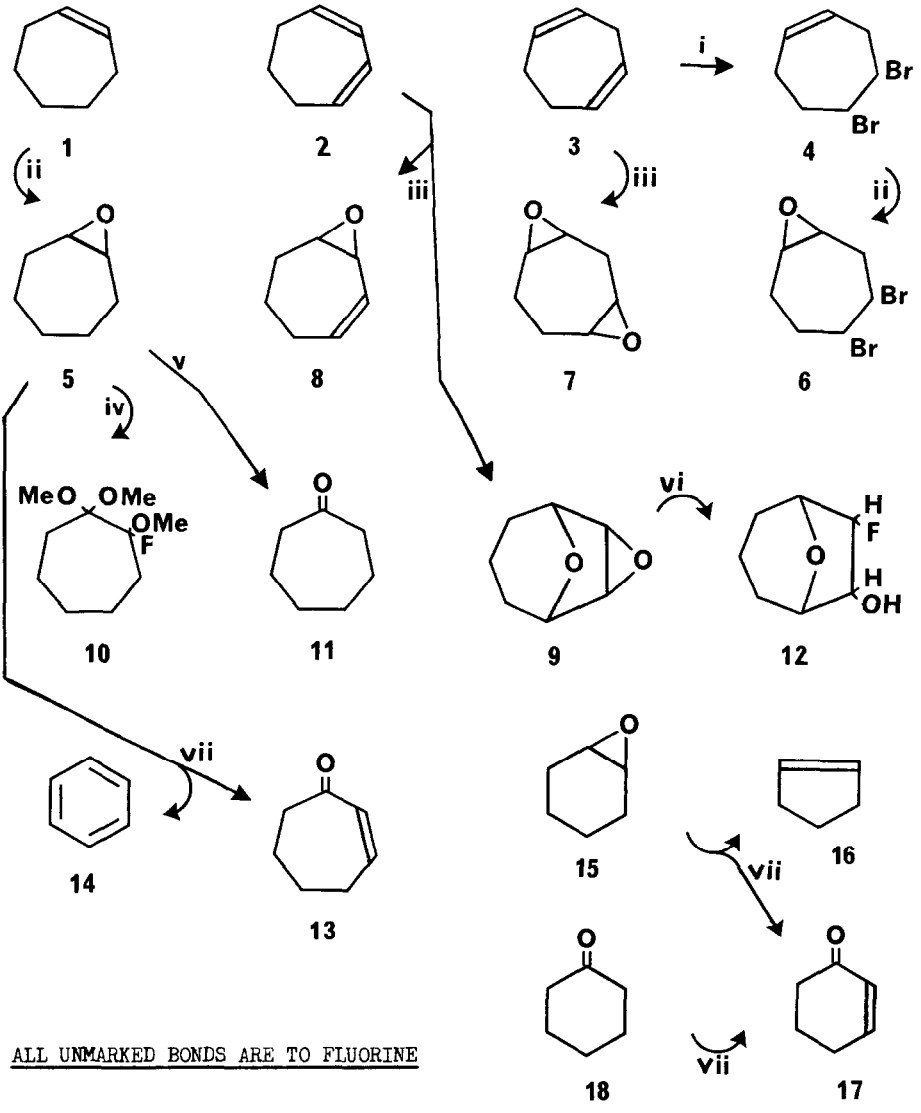
RESULTS AND DISCUSSION

The starting materials for the present work were dodecafluorocycloheptene (1, See Scheme) [5] and decafluorocyclohepta-1,3- (2) and -1,4-diene (3) [6]. Diene 3 was also converted by a standard procedure [7] to 4,5-dibromodecafluorocycloheptene (4). The mono-enes (1 and 4) were subjected to our adaptation [3] of the convenient epoxidation process [8] using aqueous sodium hypochlorite. Using acetonitrile as co-solvent, the perfluoro-ene (1) afforded dodecafluoro-1,2-epoxycycloheptane (5), and the bromo-ene (4) gave 4,5-dibromodecafluoro-1,2-epoxycycloheptane (6), both in high yield. The reactions proceeded more readily than those with comparable fluorocyclohexenes and were performed at room temperature. Presumably, the greater flexibility of the cycloheptane ring as compared with the cyclohexane ring, allows the 1,2-epoxide system to be formed in products 5 and 6 with less eclipsing of fluorine substituents than is the case with cyclohexane analogues. Products 5 and 6 had ir bands close to 1490 cm^{-1} and ^{19}F nmr peaks (due to FC-O) in the region 150-160 ppm (relative to CCl_3F) being close to the values found for epoxyfluorocyclohexanes [3].

Opening of the epoxy ring of the dodecafluoroepoxide (5) occurred with sodium methoxide. The mode of attack resembled that with decafluoro-1,2-epoxycyclohexane [4], but in the present reaction dimethyl sulphate was added before the work up. This was to methylate the anticipated product present, the alkoxide of the methyl hemi-ketal of 2-methoxyundecafluorocycloheptanone (this intermediate is of type K2, Scheme 1, Ref. [4]). In accord, the product isolated was 1,1,2-trimethoxyundecafluorocycloheptane (10). This provides further evidence in support of the general reaction pathway proposed for nucleophilic reactions of 1,2-epoxypolyfluorocycloalkanes [4].

Dodecafluoro-1,2-epoxycycloheptane (5) did not react at all readily with potassium fluoride in acetonitrile, supporting the idea of lower strain in the C7 system relative to the C6. The addition of a crown ether to the system resulted in some conversion to potassium tridecafluorocycloheptoxide, heating of which gave the known [5] dodecafluorocycloheptanone (11).

In the work on polyfluorocyclohexenes [3], the 1,4- and 1,3-dienes of that series had been oxidized to carboxylic acids by $NaOCl/H_2O/CH_3CN$, and had failed to react with sodium hypobromite, also suggested [8] to effect epoxidations. However, decafluoro-1,2-epoxycyclohepta-1,4-diene (3) was now found to react satisfactorily with aqueous sodium hypobromite containing



ALL UNMARKED BONDS ARE TO FLUORINE

Reagents: i, Br_2 ; ii, $NaOCl/H_2O/CH_3CN$; iii, $NaOBr/H_2O/CH_3CN$;
iv, NaOMe, then Me_2SO_4 ; v, KF, then heat ;
vi, $LiAlH_4$; vii, heat (500°C)

Scheme

acetonitrile to give decafluoro-(1,2)(4,5)-diepoxycycloheptane (7). This structure is allocated on the basis of spectroscopic parameters very similar to those of the mono-epoxides, including a strong absorption in the infrared at 1470-1490 cm^{-1}.

Decafluorocyclohepta-1,3-diene (2) also reacted with $NaOBr/H_2O/CH_3CN$, but a multicomponent mixture resulted. Separation by glc gave two isolatable products (8 and 9), recovered starting materials (2), and a small fraction containing unidentified components which could not be isolated pure.

The higher-boiling of the two major products (8) analysed as a mono-epoxide, had two ^{19}F nmr peaks typical of vinylic fluorine in perfluoro-cycloheptenes [5, 6], and two typical of epoxide -OCF, as well as an infrared band at 1730 cm^{-1} (-CF=CF-), and one at 1490 cm^{-1} (-CF-CF-). The structure of 8 was therefore decafluoro-1,2-epoxycyclohept-3-ene, and this was confirmed by reaction with potassium fluoride in acetonitrile to give a solid alkoxide, which decomposed on being heated to give the known [9] decafluorocyclohept-2-enone (13). Attack at either carbon of the epoxy-ring of compound 8 is possible, to give isomeric products, but only the conjugated enone (13) could be detected, perhaps not surprisingly.

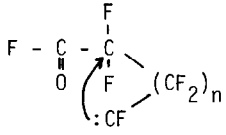
The most volatile (9) of the components had elemental analysis $C_7F_{10}O_2$, and also had the anticipated spectroscopic bands. The presence of endo- and exo- stereoisomers (4:6) was indicated. However, reaction with lithium aluminium hydride in ether showed that compound 9 was not a simple di-epoxide. This reagent readily cleaves fluorocarbon epoxy rings, with formation of -CH(OH)CHF- residues [4]. From compound 9, the cleavage product (12) analysed as $C_7H_3F_9O_2$, corresponding to loss of one epoxy ring only. Nmr showed the presence of the groups >CHOH and >CHF, but there was no infrared band corresponding to a 1,2-epoxy ring. Compound 12 is designated as 6H,7H-nonafluoro-8-oxabicyclo(3,2,1)octan-6-ol (only one stereoisomer appeared to be present [cf. 4]).

The dioxygenated product from the 1,3-diene was therefore decafluoro-6,7-epoxy-8-oxabicyclo(3,2,1)octane (9). This bicyclic oxygen-containing ring system has been encountered before [10] in polyfluorocycloheptane chemistry, and in one case a derivative based on the skeleton arose from the reaction of fuming sulphuric acid with the perfluoro-1,4-diene (3): the structure was established by X-ray analysis [11]. It is of course possible that the 1,4-diene (3) and hypochlorite ion might give rise to a tricyclic structure of the same type by formation of criss-cross bonds. However, the alkene bonds in diene 3 are independent of each other, and the

spectroscopic properties of compound 7 corresponded well with those expected from a di-(1,2-epoxy) system.

Hexafluoro-1,2-epoxypropane decomposes around 200°C to give difluorocarbene [12, 13]. However, the oxygen rings of all the polyfluoroepoxides we have studied so far [1, 2, 3] have been much more stable than this, little decomposition being detected below 300°C. Dodecafluoro-1,2-epoxycycloheptane (5) has even higher stability to heat, since flow pyrolysis over a hard glass packing had to be carried out at 500°C to give a reasonable rate of decomposition. Even so, a significant proportion of unreacted 5 was recovered, together with two known compounds, decafluorocyclohept-2-enone (13) [9] and hexafluorobenzene (14). As a comparison, decafluoro-1,2-epoxycyclohexane (15) [3] was pyrolysed under similar conditions. It also was very stable, less so than the cycloheptane homologue (5) however: at 500°C no unreacted starting material (15) was found. The products were known compounds, octafluorocyclohex-2-enone (17) [14], analogous to the C7-enone (13), and octafluorocyclopentene (16) [15]. Decafluorocyclohexanone (18) [3] was also pyrolysed, to see whether isomerisation of the epoxide (15) to this was the first step in the decomposition. Not entirely so, certainly, since pyrolysis of this saturated ketone (18) gave no octafluorocyclopentene (16), and, though the cyclohex-enone (17) was formed, much ketone 18 was recovered (none was found in the pyrolysis products of epoxide 15).

A likely first step in the decomposition pathway for both perfluoro-1,2-epoxides (5 and 15) is rupture of a C-O bond [cf. 1] to give the appropriate diradical. As a second step, these could then react with the glass packing, losing two fluorine atoms to give the conjugated enones (13 and 17). Alternatively, or perhaps concomitantly as a second stage, the C-C bond of the original epoxy-function of the diradical could break, to give a carbene.



In the cyclohexane case, insertion of the carbene function into an appropriate C-F bond could give nonafluorocyclopentyl carbonyl fluoride and thence octafluorocyclopentene (16) by loss of carbonyl fluoride. This carbene pathway seems less likely for the cycloheptane case, starting from

compound 5, since the analogous cyclo-ene, the well-known decafluorocyclohexene, was not found among the decomposition products. Complete defluorination of decafluorocyclohexene to hexafluorobenzene seems unlikely under the reaction conditions apertaining. Nonafluoro- and decafluorocyclohepta-1,3- and -1,4-dienes, when pyrolysed at 400-460°C over sodium fluoride have given significant proportions of polyfluoroarenes among the products [16]; in some cases these processes clearly involved a defluorination, as opposed to a dehydrofluorination, stage. Similar, as yet unidentified, pathways could well be used in the generation of hexafluorobenzene (14) from dodecafluoro-1,2-epoxycycloheptane (5).

EXPERIMENTAL

Bromine addition to decafluorocyclohepta-1,4-diene (3)

Diene (3) [6] (13.0 g) and bromine (40 g) in a 250 cm^3 flask fitted with a reflux condenser, were irradiated with ultraviolet light for 17 hours. After being washed with sodium metabisulphate solution to remove all bromine, the fluorocarbon layer was dried over P_2O_5 and distilled in vacuo to give 4,5-dibromodecafluorocyclohept-1-ene (4) nc (15.1 g), b.p. 93°C/10 mm Hg (Found: C, 19.5; Br, 37.0; F, 44.3. $C_7Br_2F_{10}$ requires C, 19.4; Br, 36.8; F, 43.8%); ir, 1725 cm^{-1}.

Epoxidation of dodecafluorocycloheptene (1)

Cycloheptene (1) [5] (5.0 g), treated as before [3] except that the reaction was carried out at 15°C, yielded dodecafluoro-1,2-epoxycycloheptane (5) nc (4.5 g), b.p. 101°C (Found: C, 25.7; F, 69.6. $C_7F_{12}O$ requires C, 25.6; F, 69.5%); ir, 1485 cm^{-1}.

Epoxidation of 4,5-dibromodecafluorocycloheptene (4)

Bromo-ene (4) (10.0 g), treated as above, afforded 4,5-dibromodecafluoro-1,2-epoxycycloheptane (6) nc (9.3 g), b.p. 86°C/10 mm Hg, m.p. 25°C (Found: C, 19.0; Br, 35.8; F, 42.3. $C_7Br_2F_{10}O$ requires C, 18.7; Br, 35.5; F, 42.2%); ir, 1490 cm^{-1}.

Epoxidation of decafluorocyclohepta-1,4-diene (3)

The 1,4-diene (3) [6] (10.0 g) was added to a stirred mixture of freshly prepared sodium hypobromite solution (200 cm^3) [17] and acetonitrile (100 cm^3) at 0°C. The mixture was stirred for 1 hour at 0°C, water (300 cm^3) added, and the lower layer separated, dried ($MgSO_4$) and distilled, to give deca-

fluoro-(1,2)(4,5)-diepoxycycloheptane (7) nc (7.3 g), b.p. 87°C (Found: C, 27.4; F, 62.4. $C_7F_{10}O_2$ requires C, 27.5; F, 62.1%); ir, 1470, 1490 (double peak) cm^{-1}.

Epoxidation of decafluorocyclohepta-1,3-diene (2)

The 1,3-diene (2) [6] (20.0 g) was added to a stirred mixture of sodium hypobromite solution (150 cm^3) and acetonitrile (25 cm^3) at 0°C. After being stirred for 2 hours at 0°C, the mixture was diluted with water, the lower layer separated and dried ($MgSO_4$). Separation by preparative glc [copper tube, 4.8 m x 35 mm int. diam.; packing dinonyl phthalate/Chromosorb P30-60 (1:5); 85°C; N_2 12 lh^{-1}] afforded: (i), after 30 min., decafluoro-6,7-epoxy-8-oxabicyclo(3,2,1)octane (9) nc (3.3 g), b.p. 79°C (Found: C, 27.2; F, 62.0. $C_7F_{10}O_2$ requires C, 27.5; F, 62.1%); ir, 1475 cm^{-1}; (ii), after 50 min., decafluoro-1,2-epoxycyclohept-3-ene (8) nc (6.5 g), b.p. 85°C (Found: C, 28.9; F, 65.9. $C_7F_{10}O$ requires C, 29.0; F, 65.5%); ir, 1490, 1730 cm^{-1}; (iii), after 80 min., recovered (2) 2.0 g: (iv), 100-140 min., 3 unidentified components (0.6 g).

Action of sodium methoxide on dodecafluoro-1,2-epoxycycloheptane (5)

A solution of compound 5 (10.0 g) in dry diethyl ether (10 cm^3) was added to a stirred solution made by adding sodium (3.5 g) to dry methanol (50 cm^3). After being stirred for 12 hours at 15°C, the mixture was treated with dimethyl sulphate (2 g), and stirring was continued for 2 hours more. Water (100 cm^3) was added, the ether layer and extracts of the aqueous layer were combined, dried ($MgSO_4$) and the bulk of the ether distilled off. The residue was washed with dilute aqueous sodium hydroxide, then water, dried ($MgSO_4$) and distilled in vacuo to give 1,1,2-trimethoxy-undecafluorocycloheptane (10) nc (3.8 g), b.p. 203°C (Found: C, 30.8; H, 2.4; F, 53.7. $C_{10}H_9F_{11}O_3$ requires C, 31.1; H, 2.3; F, 54.1%).

Action of potassium fluoride on dodecafluoro-1,2-epoxycycloheptane (5)

Epoxide 5 (6.0 g), potassium fluoride (1.2 g) and ether 18-Crown-6 (0.1 g) in dry acetonitrile (30 cm^3) were stirred together at 15°C for 56 hours. The volatile components (A) were removed by distillation in vacuo to leave a solid (B). Water was added to condensate (A), and the lower layer separated and dried to give recovered 5 (2.3 g). Solid residue B was heated in vacuo until it had decomposed. The condensate (1.2 g) was dodecafluoro-cycloheptanone (11), b.p. 86°C (cited [5] 85-86°C) with a correct infrared spectrum.

Reaction of lithium aluminium hydride with decafluoro-6,7-epoxy-8-oxa-bicyclo(3,2,1)octane (9)

Compound 9 (3.0 g) was added to a suspension of lithium aluminium hydride (0.5 g) in dry diethyl ether (25 cm^3), and the mixture stirred at 15°C for 16 hours. Water (5 cm^3) was added cautiously, followed by dilute sulphuric acid (2M, 20 cm^3). The ether layer and extracts were dried ($MgSO_4$) and the bulk of the ether distilled off through a short fractionating column. The residue was purified by glc [Pye Series 104 instrument, column 9.1 m x 7 mm int. diam., packed with silicone gum SE30/supasorb 60-80 (1:9); 150°C; N_2 1.5 lh^{-1}] to give 6H,7H-nonafluoro-8-oxabicyclo(3,2,1)-octan-6-ol (12) nc (1.2 g), b.p. 171°C (Found: C, 28.4; H, 1.3. $C_7H_3F_9O_2$ requires C, 29.0; H, 1.0%).

Reaction of potassium fluoride with decafluoro-1,2-epoxycyclohept-3-ene (8)

The epoxy-ene (8) (3.2 g), potassium fluoride (0.8 g) and acetonitrile (25 cm^3) were stirred together at 30°C for 30 min. The solvent was then evaporated off and the solid residue heated in vacuo to give decafluorocyclohept-2-enone (13) (1.4 g) [9] with correct glc retention time, and infrared spectrum.

Pyrolysis experiments

These were carried out by passage through a vertical Pyrex glass tube (600 mm x 20 mm int. diam.) packed with pieces of Pyrex tubing (10 mm x 6 mm int. diam), and heated to 500°C by electrical heating bricks. Products were collected in traps cooled by liquid air, washed with water, dried ($MgSO_4$) and separated by glc [tube 4.8 m x 35 mm int. diam.; packing, dinonyl phthalate/Chromosorb P30-60 (1:5); temp. 85°C; N_2 flow rate stated below].

(a) Dodecafluoro-1,2-epoxycycloheptane (5). Compound 5 (15.0 g) was passed into the column in a stream of dry nitrogen (1 lh^{-1}) during 30 min. Products (9.0 g) by glc (N_2, 20 lh^{-1}) were: (i), unreacted epoxide (5) (2.6 g); (ii), decafluorocyclohept-2-enone (13) [9] (1.7 g); (iii), hexafluorobenzene (14) (3.4 g); all had correct glc retention times and infrared spectra, and fraction (ii) had a correct ^{19}F nmr spectrum.

(b) Decafluoro-1,2-epoxycyclohexane (15). Compound 15 (10.0 g; N_2 stream 2 lh^{-1}; reaction otherwise as in (a) gave by glc (N_2, 15 lh^{-1}): (i), octafluorocyclopentene (16) [15] (3.7 g); (ii), octafluorocyclohex-2-enone (17) [14] (2.2 g); both had correct glc and infrared data.

(c) Decafluorocyclohexanone (18) Ketone 18 [3] (6.0 g; N_2 stream 1 lh^{-1}; passage time 20 min.) gave by glc (N_2, 20 lh^{-1}): (i), unreacted decafluorocyclohexanone (18) (2.1 g); (ii), octafluorocyclohex-2-enone (1.7 g); both were identified by glc and ir.

Spectroscopy

Infrared spectra were recorded as liquid films on a Perkin Elmer 257 instrument.

Nmr spectra were recorded on a Perkin Elmer R12B spectrometer (^1H at 60 MHz, with tetramethylsilane as internal reference, ^{19}F at 56.4 MHz, with trichlorofluoromethane as internal reference). Unless otherwise stated measurements were done on 10-20% w/v solutions in deuterochloroform. Results are recorded in the Table (b = broad, c = complex, d = doublet, m = multiplet, s = singlet, t = triplet).

TABLE

Nmr Spectra of Compounds Synthesised

Compound Number	Chemical Shifts	Relative Intensity	Position in Formula	Type of Signal and Couplings
4 F	93.0-130.7	8	3,4,5,6,7	c
	135.6	1	1,2	cm
	140.7	1		cm
5 F	120.1	1	3,4,5,6,7	cm
	123.1	1		cm
	127.8	1		cd, Jd = 98
	128.2	1		cm
	130.4	1		cm
	158.8	1	1,2	cm
6 F	94.5-131.2	8	3,4,5,6,7	c
	150.5	0.3	1,2	cm
	155.4	0.7		cm
	157.8	1		cm

(Continued overleaf)

TABLE (Cont.)

Compound Number	Compound Shifts	Relative Intensity	Position in Formula	Type of Signal and Couplings
7 F	115.1	1	3	t, J = 14
	122.7	1	6,7	cm
	124.4	1		cm
	156.4	1	1,2,4,5	cm
	157.9	1		cm
8 F	114.7	2	5	AB, J = 302, $\Delta\gamma$ = 578
	123.5	2	6,7	cm
	128.2	2		cm
	144.1	1	3	dd, J = 75, J = 21
	144.0	1	4	dt, Jd = 75, Jt = 23
	151.5	1	2	cm
	158.8	1	1	cm
9 F	121.9	2	2,4	cm
	128.3	1	3	cm
	156.2	0.4	6,7 endo	d, J = 9
	156.6	0.6	6,7 exo	t, J = 8
	157.7	1	1,5	cm
10 F	110.6	1	3,4,5,6,7	cm
	111.1	1		cm
	113.6	1		cm
	115.6	1		cm
	117.6	1		cm
	118.6	3		cm
	120.2	2		cm
	135.6	1	2	cm
H	3.02	2	1 (OCH_3)	cm
	3.13	1	2 (OCH_3)	cm
11 F	121.1	1	2,7	cm
	129.8	2	3,4,5,6	cm

(Continued on facing page)

TABLE (Cont.)

Compound Number	Chemical Shifts	Relative Intensity	Position in Formula	Type of Signal and Couplings
12 F (Neat)	115.6-132.5	6	2,3,4	c
	147.2	1	1,5	cm
	161.9	1	1,5	cm
	214.1	1	7	cm
H	4.30	1	6 CH	bm
	4.47	1	6 OH	bs
	5.36	1	7	cd, Jd = 45

REFERENCES

1 Part IV of this Series: P.L. Coe, A. Sellars, J.C. Tatlow, H.C. Fielding and G. Whittaker, J. Fluorine Chem., 27, (1985) 71.

2 P.L. Coe, A. Sellars and J.C. Tatlow, J. Fluorine Chem., 23 (1983) 102.

3 P.L. Coe, A.W. Mott and J.C. Tatlow, J. Fluorine Chem., 20 (1982) 243.

4 P.L. Coe, A.W. Mott and J.C. Tatlow, J. Fluorine Chem., 20 (1982) 659.

5 J.A. Oliver, R. Stephens and J.C. Tatlow, J. Fluorine Chem., 22 (1983) 21.

6 A.E.M.M. Khalil, R. Stephens and J.C. Tatlow, J. Fluorine Chem., 22 (1983) 31.

7 D.E.M. Evans and J.C. Tatlow, J. Chem. Soc., (1954) 3779.

8 I.P. Kolenko, T.I. Filyakova, A.Ya. Zapevalov and E.P. Lur'e, Izvest. Akad. Nauk. S.S.S.R., Ser. Khim., (1979) 2509.

9 C.M. Jenkins, R. Stephens and J.C. Tatlow, J. Fluorine Chem., 25 (1984) 233.

10 D.J. Dodsworth, C.M. Jenkins, R. Stephens and J.C. Tatlow, J. Fluorine Chem., 24 (1984) 509.

11 M.J. Hamor, T.A. Hamor, C.M. Jenkins, R. Stephens and J.C. Tatlow, J. Fluorine Chem., 10 (1977) 605.

12 E.P. Moore, U.S.P. 3,338,978 (1967).

13 P. Tarrant, C.G. Allison, K.P. Barthold and E.C. Stump, Fluorine Chem. Reviews, 5 (1971) 77.

14 R.G. Plevey, D.J. Sparrow and J.C. Tatlow, J. Fluorine Chem., 26 (1984) 515.

15 R.J. Heitzman, C.R. Patrick, R. Stephens and J.C. Tatlow, J. Chem. Soc., (1963) 281.

16 D.J. Dodsworth, C.M. Jenkins, R. Stephens and J.C. Tatlow, J. Fluorine Chem., 24 (1984) 41.

17 J. Stainton and E.J. Eisenbraun, Organic Synthesis, Coll. Vol. 5 (1973) 9.