Valence-bond isomer chemistry. Part 13*. Photochemical oxidation of hexafluorobenzene: formation of hexafluoro-3-oxatricyclo[3.2.0.0^{2,4}]hept-6-ene and its reactions

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Abstract

Vapour-phase ultraviolet irradiation of hexafluorobenzene in the presence of oxygen slowly yields hexafluoro-3-oxatricyclo[3.2.0.0^{2,4}]hept-6-ene (**2**) (10%). The CF=CF bond in **2** adds (yields of adducts given) the dienes; cyclopentadiene (74%), furan (61%) and 2,5-diphenylisobenzofuran (59%); benzonitrile oxide (58%); chlorine (59%) and bromine (71%) photochemically. Heptene **2** isomerises thermally to hexafluorocyclohexa-2,4-dienone (**6**) (60%) at 50 °C, and reacts with diethyl ether at room temperature yielding ethyl fluoride (89%) and 2-ethoxypentafluorocyclohexa-2,5-dienone (21%). The benzonitrile oxide adduct, upon flow pyrolysis at 440 °C, yields an isomeric oxepin derivative and the cyclohexadienone **6** with longer contact times. The chlorine adduct similarly yields a dichloro-oxepin derivative; attempts to dechlorinate this to hexafluoro-oxepin were unsuccessful. Benzonitrile oxide adds to one or both of the C=C bonds of hexafluorobicyclo[2.2.0]hexa-2,5-diene; the 1:1 adduct isomerises thermally to the benzonitrile oxide–hexafluorobenzene adduct.

Introduction

Ultraviolet irradiation of hexafluorobenzene in the vapour phase yields the valence-bond isomer, hexafluorobicyclo[2.2.0]hexa-2,5-diene (**1**) (hexafluoro-Dewar-benzene) [2]. We had noted that oxygen had a beneficial effect upon the yield of the Dewar benzene when light of $\lambda > 200$ nm was used, but on occasion small amounts of an oxygen-containing compound of similar volatility were detected. Further investigation has led to its identification as hexafluoro-3-oxatricyclo[3.2.0.0^{2,4}]hept-6-ene (**2**), an isomer of the hexafluorobenzene oxide–hexafluoro-oxepin system, which prompted further study.

Results and discussion

Ultraviolet irradiation ($\lambda > 200$ nm) of a gaseous mixture of hexafluorobenzene, oxygen (200 mmHg) and nitrogen (300 mmHg) resulted in a rapid

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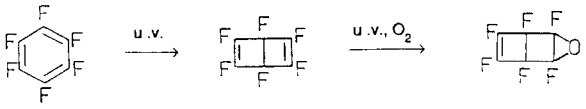
isomerisation of the benzene to its isomer, Dewar benzene (**1**), and much more slowly to the formation of the Dewar-benzene oxide (**2**), the yield being about 10% after 75 h irradiation (Scheme 1). Much oxygen-containing, polymeric material was also formed, and this tended to coat the silica insert containing the lamp, cut out the shorter wavelength ultraviolet light and prevent the formation of **2**. Fluoro-olefins undergo photo-oxidation to epoxides via a complex chain reaction which involves transfer of an oxygen atom from a perfluoroalkylperoxy radical to a fluoro-olefin molecule [3]. Presumably a similar oxidation of Dewar-benzene (**1**) is involved here; indeed, irradiation



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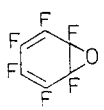
Scheme 1.



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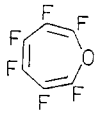

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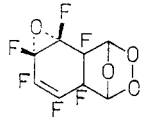

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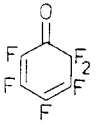

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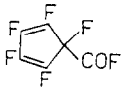

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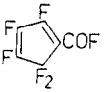

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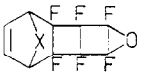
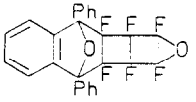


(**11**; X = CH_2)
(**12**; X = O)



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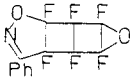


(14)

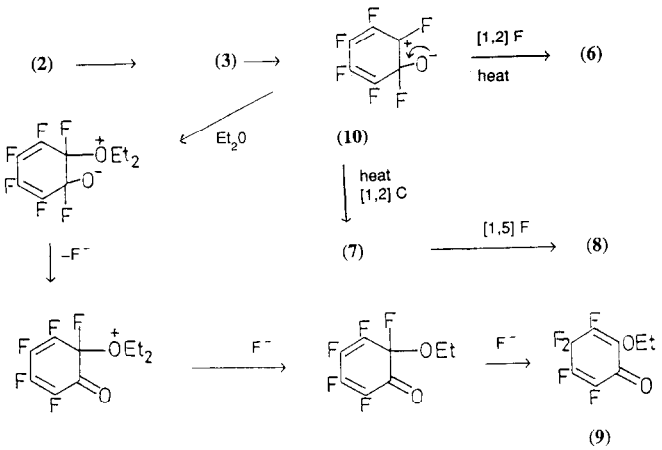
of **1** in the presence of oxygen resulted in a more rapid formation of the oxide **2**.

The elegant work of Vogel and his co-workers has revealed that benzene oxide and its valence-bond isomer, oxepin, are in rapid equilibrium [4], with the equilibrium evenly balanced [5]. The availability of the oxide **2** prompted attempts to obtain the hexafluoro analogues **3** and **4**, but these were unsuccessful. Recently, Lemal *et al.* have described a synthesis of the rather labile hexafluorobenzene oxide (**3**), using photochemical decomposition of the ozonide **5** as the final step; it rearranged readily to hexafluorocyclohexa-2,4-dienone (**6**) in polar solvents, or upon warming [6].

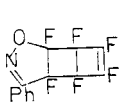
The oxide **2** when heated at 50 °C for 7 d gave the dienone **6** (60%) as the only volatile product. Flow pyrolysis at 275 °C in silica with a short (0.5 μs) contact time yielded the dienone **6** (72%), together with the isomeric acid fluorides **7** (12%) and **8** (7%) (identified spectroscopically) and small amounts of other acid fluorides. The oxide **2** reacted slowly with diethyl ether at room temperature, forming ethyl fluoride (89%) and pentafluoro-2-ethoxycyclohexa-2,5-dienone (**9**). All of these observations can be accounted for (see Scheme 2) in terms of the isomerisation of oxide **2** to hexafluorobenzene oxide (**3**), and ring opening to form a dipolar intermediate **10** which can undergo 1,2-shift of fluorine to give **6** or of carbon to give acid fluoride **7** and thence **8** by [1,5]-sigmatropic shift of fluorine. Zwitterion **10** is trapped by diethyl ether, when ethyl fluoride and 2-ethoxypentafluocyclohexa-2,5-dienone (**9**) result (see Scheme 2). Alternatively, a diradical intermediate analogous to **10** may be involved, particularly for the gas-phase isomerisation.

Hexafluorobicyclo[2.2.0]hexa-2,5-diene (**1**) undergoes ready addition of dienes [7] and 1,3-dipoles [8, 9] to the strained C=C bonds. Its oxide **2** possesses a similar strained double bond and undergoes ready addition of the dienes cyclopenta-1,3-diene, furan and 2,5-diphenyl isobenzofuran at room temperature to give the adducts (**11**; 74%), (**12**; 61%) and (**13**; 59%), respectively. Benzonitrile oxide gave the adduct **14**. For comparison, addition of benzonitrile oxide in portions to Dewar-benzene (**1**) at 0 °C gave the 1:1 adduct (**15**; 65%) and 2:1 adducts **16** and **17**.

Chlorine and bromine add in the dark to one of the C=C bonds of Dewar-benzene (**1**), but addition to the second C=C bond requires photochemical initiation, and *exo* addition is favoured [10]. The oxide **2** failed to react with chlorine or bromine in carbon tetrachloride in the dark, but gave a mixture of *cis*, *exo*- and *trans*-dihalides (**18**) and (**19**) when visible light was used to initiate the reaction. This difference in reactivity between the Dewar benzene (**1**) and its oxide (**2**) enabled an easy separation of these two compounds, since compound **1** could be selectively brominated. The mixture of dichlorides when subjected to brief pyrolysis at 415 °C (contact time *c.* 2 ms) gave a *cis/trans* mixture of dichloro-oxepin derivatives (**20**; 66%), but the dibromides gave bromine and a very complex mixture of products under comparable conditions. The dichloro-oxepin **20** offered the possibility of dechlorination to hexafluoro-oxepin (**4**), but attempts to do so failed to yield material of the appropriate volatility. Lemal *et al.* have found



Scheme 2.



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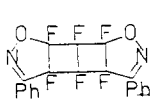

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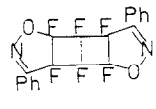

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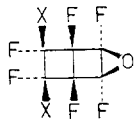
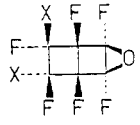
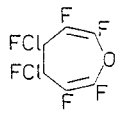


(18a, X = Cl; b, X = Br)



(19a, X = Cl; b, X = Br)



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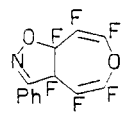


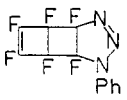
(21)

that the benzene oxide **3** is reduced under very mild conditions to pentafluorophenol [6], so our failure is not surprising.

The ease of formation of oxepin derivatives such as **20** prompted a study of the thermolysis of the benzonitrile oxide adduct **14**: this, when passed through a silica tube at 440 °C with a contact time of *c.* 8 ms, gave the expected ring-opened isomer (**21**; 52%), a 1,3-dipole adduct of hexafluorooxepin. When the contact time was increased to *c.* 42 s, the hexadienone **6** and 3,4-diphenylfuroxan were formed.

Thermolysis of the phenylazide adduct **22** of hexafluorobicyclo-[2.2.0]hexa-2,5-diene (**1**) results in loss of nitrogen and formation of the azepine **23** [11]. The benzonitrile oxide adduct **15** was studied to see if an analogous elimination of benzonitrile would occur. However, heating the

adduct under static (160 °C) or flow conditions (450 °C, 5 ms) resulted in ring opening to give the hexafluorobenzene–benzonitrile oxide adduct (**24**) in high yield, and a long contact time resulted in formation of hexafluorobenzene and the nitrile oxide dimer.



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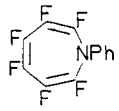

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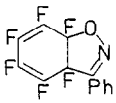

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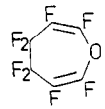

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In the hexafluorobenzene oxide–hexafluoro-oxepin system, the equilibrium strongly favours the benzene oxide [6], which contrasts with the case of azepines such as **23**, where no bicyclic isomer was detected [11]. Our failure to obtain the benzene oxide is understandable in light of its lability [6].

Experimental

General techniques

Volatile materials were manipulated in a Pyrex vacuum system and product mixtures were separated by trap-to-trap distillation *in vacuo* or by gas–liquid chromatography (GLC). Products were identified by elemental analysis, infrared spectroscopy (IR) (Perkin-Elmer models 257 or 397), nuclear magnetic resonance spectroscopy [Perkin-Elmer R32 operating at 90 MHz for ^{1}H spectra (tetramethylsilane reference) and 84.6 MHz for ^{19}F nuclei (external trifluoroacetic acid reference)], low-resolution mass spectrometry (electron impact at 70 eV on a Kratos MS45 instrument), and GLC [Pye 104 (modified for preparative separations) or Pye Unicam model GCD instruments]. Molecular weights were obtained from the mass spectra data.

Melting points are reported uncorrected.

Attempted oxidation of hexafluorobicyclo[2.2.0]hexa-2,5-diene (1)

(a) With oxygen

A 1 l Pyrex bulb, with mercury manometer and tapped inlet, containing hexafluorobicyclo[2.2.0]hexa-2,5-diene (0.52 g, 2.8 mmol), was pressurised to 1 atm with dry oxygen and shaken behind a heavy blast screen for 4 weeks. The volatile material (0.272 g) was then shown by GLC and ^{19}F NMR methods to comprise hexafluorobenzene (39 mg, 0.2 mmol, 7%) and unchanged

diene (0.233 g, 1.3 mmol, 45%). The involatile solid which remained in the bulb was not examined.

(b) With hydrogen peroxide

To a solution of potassium hydroxide (0.66 g, 11.5 mmol) in methanol (3.1 cm^3), contained in a Rotaflo tapped ampoule (10 cm^3) at −50 °C, was added hydrogen peroxide (1.1 cm^3 of a 50% w/v solution, 16 mmol), followed by hexafluorobicyclo[2.2.0]hexa-2,5-diene (2.0 g, 10.8 mmol). The mixture was then shaken at −50 °C for 3 h, warmed to room temperature over 15 min, and the volatile material removed *in vacuo* and fractionated by trap-to-trap distillation to give unreacted diene (1.1 g, 5.9 mmol, 55%), which condensed at −45 °C, and a mixture of water and methanol which condensed at −196 °C. The solid that remained in the ampoule was washed out with chloroform, but when the chloroform was removed under reduced pressure it exploded.

Preparation of hexafluoro-3-oxatricyclo[3.2.0.0^{2,4}]hept-6-ene (2)

To an evacuated 20 l Pyrex flask, fitted with a water-cooled silica insert containing a Hanovia UVS 500 mercury lamp, a mercury manometer and a tapped ampoule, was admitted oxygen (200 mmHg) and nitrogen (300 mmHg), followed by hexafluorobenzene (35.0 g, 188 mmol). The mixture was irradiated for 75 h and the flask was then evacuated through two traps cooled to −78 °C and −196 °C, leaving involatile polymeric material (18.5 g).

The −196 °C trap contained carbonyl fluoride (25.1 mmol), identified by IR spectroscopy [12]. To the contents of the −78 °C trap (14.8 g), shown by GLC methods (2 m SE30 on Celite at 25 °C) to comprise hexafluorobenzene (42.3 mmol, 23%), hexafluorobicyclo[2.2.0]hexa-2,5-diene (**1**) (16.0 mmol, 9%) and hexafluoro-3-oxatricyclo[3.2.0.0^{2,4}]hept-6-ene (**2**) (19.6 mmol, 10%), was added bromine dropwise at 0 °C in subdued light until a slight colour of bromine persisted. The excess of bromine was removed with mercury, and the mixture was fractionated by trap-to-trap distillation to give a mixture (by ^{19}F NMR and GLC methods) of hexafluorobenzene and 5,6-dibromohexafluorobicyclo[2.2.0]hex-2-ene [10] which condensed at −23 °C, and a mixture of hexafluorobenzene and hexafluoro-3-oxatricyclo[3.2.0.0^{2,4}]hept-6-ene (**2**) which condensed at −78 °C. The latter fraction was separated by GLC (4 m APL on Celite at 30 °C) to give hexafluoro-3-oxatricyclo-[3.2.0.0^{2,4}]hept-6-ene (**2**) (nc) (2.24 g, 11.1 mmol, 6%) (Analysis: Found: C, 35.4; F, 56.1%; mol wt., 202. C_6F_6O requires: C, 35.7; F, 56.4%; mol wt., 202) as a colourless liquid. ^{19}F NMR (50% in hexafluorobenzene) δ: −43.3 (F-6 and -7); −97.0 (F-2 and -4); and −119.0 (F-1 and -5) ppm. IR ν_{max} (cm^{-1}): 1755 (C=C str.); and 1550 (epoxide ring str.). Mass spectrum *m/z* (>10%): 202 (60.8%, M^+); 174 (40.9, $C_5F_6^+$); 155 (39.7, $C_5F_5^+$); 124 (100.0, $C_4F_4^+$); 105 (14.1, $C_4F_3^+$); 93 (21.9, $C_3F_3^+$); 74 (11.5, $C_3F_2^+$); 69 (30.1, CF_3^+); 31 (22.4, CF^+); and 28 (22.3, CO^+).

It was essential to clean the silica insert thoroughly between runs. It was washed free of polymeric material with ethanol, rinsed with distilled

water, steeped in chromic acid solution at 170 °C for 3 h, rinsed with water, steeped in a 15% w/v solution of Decon 90 at 100 °C for 18 h and washed with water.

*Reactions of hexafluoro-3-oxatricyclo[3.2.0.0^{2,4}]hept-6-ene (**2**)*

(a) With cyclopenta-1,3-diene

The title heptene (0.168 g, 0.83 mmol) and cyclopenta-1,3-diene (0.300 g, 4.5 mmol) in diethyl ether (1.5 g) were sealed *in vacuo* in a tapped Pyrex ampoule (5 cm^3) and shaken at room temperature for 1.5 h. Volatile material was removed *in vacuo* at 0 °C and the solid residue was sublimed at 24 °C/0.6 mmHg to give 2,3,4,6,7,8-hexafluoro-5-oxapentacyclo-[7.2.1.0^{2,8}0.^{3,7}0^{4,6}]dodec-10-ene (**11**) (nc) (0.163 g, 0.61 mmol, 74%) (Analysis: Found: C, 49.3: H, 2.3; F, 42.5%; mol wt., 268. $C_{11}H_6F_6O$ requires: C, 49.3; H, 2.2; F, 42.5%; mol. wt., 268) as a white solid (m.p., 62 °C). ^{1}H NMR (30% in $CDCl_3$) δ: 6.52 (H-10 and -11); 3.43 (H-1 and -9); and 1.65 (H-12) ppm. ^{19}F NMR δ: −96.4; −98.4; and −116.7 (all 2F) ppm. IR ν_{max} (cm^{-1}): 1540 (epoxide ring str.). Mass spectrum *m/z*: 268 (1.0%, M^+) and (>5%) 202 (7.0, $C_6F_6O^+$); 201 (8.5, $C_{10}H_5F_4^+$); 200 (6.4, $C_{10}H_4F_4^+$); 174 (6.5, $C_5F_6^+$); 169 (9.9, $C_9H_4F_3^+$); 155 (6.1, $C_5F_5^+$); 151 (14.4, $C_6H_3F_4^+$); 128 (7.6, $C_4H_4F_4^+$); 127 ($C_7H_5F_2^+$); 124 (6.2, $C_4F_4^+$); 102 (15.4, $C_5H_4F_2^+$); 95 (6.7, $C_6H_4F^+$); 77 (5.8, $C_6H_5^+$); 75 (5.7, $C_6H_3^+$); 69 (6.9, CF_3^+); 66 (100.0, $C_5H_6^+$); 65 (15.4, $C_5H_5^+$), 51 (7.5, $C_4H_3^+$); and 39 ($C_3H_3^+$).

(b) With furan

The title heptene (69.3 mg, 0.34 mmol) and furan (132 mg, 1.9 mmol) were sealed *in vacuo* in an NMR tube for 3 d at room temperature when reaction was complete (as ascertained by ^{19}F NMR spectroscopy). Volatile material was removed *in vacuo* at −10 °C and the residue sublimed at 35 °C/0.1 mmHg to give 2,3,4,6,7,8-hexafluoro-5,12-dioxapentacyclo-[7.2.1.0.^{2,8}0.^{3,7}0^{4,6}]dodec-10-ene (**12**) (nc) (56.7 mg, 0.21 mmol, 61%) (Analysis: Found: C, 44.4; H, 1.8; F, 41.7%. $C_{10}H_4F_6O_2$ requires: C, 44.4; H, 1.5; F, 42.2%) as a white solid (m.p., 66 °C). ^{1}H NMR (30% w/v $CDCl_3$) δ: 6.75 (H-10 and -11); and 5.28 (H-1 and -9) ppm. ^{19}F NMR δ: −103.1; −105.2; and −118.0 (all 2F) ppm. IR ν_{max} (cm^{-1}): 1540 (epoxide ring str.).

(c) With 2,5-diphenylisobenzofuran

The title heptene (132 mg, 0.65 mmol) and 2,5-diphenylisobenzofuran (118 mg, 0.44 mmol) in n-pentane (*c.* 2.5 cm^3) sealed in a Pyrex ampoule and shaken at room temperature for 7 d gave, after removal of volatile material *in vacuo*, a residue which was recrystallised from n-pentane to give 2,3,4,6,7,8-hexafluoro-1,9-diphenyl-5,12-dioxa-10,11-benzopentacyclo-[7.2.1.0.^{2,8}0.^{3,7}0^{4,6}]dodec-10-ene (**13**) (nc) (123 mg, 0.26 mmol, 59%) (Analysis: Found: C, 65.9; H, 2.9; F, 24.1%; mol. wt., 472. $C_{26}H_{14}F_6O_2$ requires: C, 66.1; H, 3.0; F, 24.1%; mol wt., 472) as a white solid (m.p., 155–157 °C (dec.)). ^{19}F NMR (25% w/v in Et_2O) δ: −98.0; 108.0; and −119.5 (all 2F) ppm. IR ν_{max} (cm^{-1}): 1547 (epoxide ring str.).

(d) With benzonitrile oxide

An ethereal solution of benzonitrile oxide, prepared from phenylhydroxamic acid chloride (0.53 g, 3.4 mmol) in diethyl ether (5 cm^3) and aqueous sodium hydroxide, was added at 0 °C to a solution of the title heptene (0.35 g, 1.7 mmol) in diethyl ether (5 cm^3) containing anhydrous $MgSO_4$ (0.4 g), and the mixture was shaken at room temperature for 18 h. Volatile material was then removed *in vacuo* and the residue sublimed at 55 °C/0.1 mmHg to give 1,2,3,5,6,7-hexafluoro-8-phenyl-4,10-dioxa-9-aza-tetracyclo[5.3.0.0.^{2,6}0^{3,5}]dec-8-ene (**14**) (nc) (0.31 g, 1.0 mmol, 58%) (Analysis: Found: C, 48.6; H, 1.3: N, 4.4%; mol. wt., 321. $C_{13}H_5F_6NO_2$ requires: C, 48.6, H, 1.6; N, 4.4%: mol. wt., 321) as a white solid (m.p., 57–58 °C). ^{19}F NMR (30% w/v in $CDCl_3$) δ: −45.0 (F-1); −85.5 (F-7); −97.0; −98.5 (F-3 and -5); −105.7; and −110.5 (F-2 and -6) ppm. IR ν_{max} (cm^{-1}): 1545 (epoxide ring str.).

(e) With chlorine

The title heptene (0.300 g, 1.5 mmol) and chlorine (0.42 g, 5.9 mmol) in carbon tetrachloride (3.0 g) were sealed in a Pyrex ampoule (250 cm^3) and irradiated with light from a 150 W tungsten filament lamp at a distance of 0.5 m for 20 h. Volatile material was removed *in vacuo* through two traps cooled to −64 and −196 °C, leaving an involatile residue (0.15 g). the −196 °C trap contained chlorine. The contents of the −64 °C trap were separated by GLC methods (10 m SE30 on Celite at 70 °C) to give carbon tetrachloride and a 3.4:1 mixture of *cis*, *exo*- and *trans*-6,7-dichlorohexafluoro-3-oxatricyclo[3.2.0.0^{2,4}]heptane (**18a** and **19a**) (0.238 g, 0.9 mmol, 59%) (Analysis: Found: C, 26.2; Cl, 26.0%; mol wt., 272. $C_6Cl_2F_6O$ requires: C, 26.4; Cl, 26.0%; mol. wt., 272) as a colourless liquid. ^{19}F NMR (in CCl_4) δ: *cis* isomer, −39.0 (F-6 and -7); −102.3 (F-2 and -4); and −107.7 (F-1 and -5); *trans* isomer, −36.2 (*exo*-F-6); −40.8 (*endo*-F-7); −98.0 (F-4); −104.4 (F-2); −105.9 (F-1); and −117.6 (F-5) ppm. IR ν_{max} (cm^{-1}): 1558 (epoxide ring str.).

(f) With bromine

The title heptene (0.260 g, 1.29 mmol) and bromine (0.720 g, 4.51 mmol) in carbon tetrachloride (2.5 g), sealed in a Pyrex ampoule (100 cm^3) and irradiated with light from a 150 W tungsten filament lamp at a distance of 0.5 m for 20 h, gave after removal of the excess of bromine with mercury and separation by GLC methods (10 m SE30 on Celite at 100 °C) a 4.3:1 mixture of *cis*, *exo*- and *trans*-6,7-dibromohexafluoro-3-oxatricyclo-[3.2.0.0^{2,4}]heptane (**18b** and **19b**) (0.350 g, 0.92 mmol, 71%) (Analysis: Found: C, 19.6; F, 31.1%; mol. wt., 362. $C_6Br_2F_6O$ requires: C, 19.9; F, 31.5%; mol. wt. 360). ^{19}F NMR of *cis* isomer (30% w/v in CCl_4) δ: −36.0 (F-6 and -7); −95.7 (F-2 and -3); and −98.7 (F-1 and -5) ppm. IR ν_{max} (cm^{-1}) 1550: (epoxide ring str.).

(g) With diethyl ether

The title heptene (113 mg, 0.56 mmol) and diethyl ether (122 mg, 1.7 mmol) were sealed in an NMR tube and the mixture examined periodically by ^{19}F NMR spectroscopy. After 90 d when none of the heptene remained, the volatile material was removed leaving an unidentified residue (22 mg), and then fractionated by trap-to-trap distillation *in vacuo* to give ethyl fluoride (24 mg, 0.50 mmol, 89%) which condensed at −196 °C, diethyl ether (30 mg, 0.41 mmol) which condensed at −95 °C, and a mixture (105 mg) which condensed at −64 °C. This last fraction was separated by GLC methods (4 m SE30 on Celite at 110 °C) to give diethyl ether (10 mg) and pentafluoro-2-ethoxycyclohexa-2,5-dienone (**9**) (nc) (28 mg, 0.12 mmol, 21%) (Analysis: Found: C, 42.2; H, 2.3: F, 41.6%. $C_8H_5F_5O_2$ requires: C, 42.1; H, 2.2; F, 41.6%) as a colourless liquid. ^1H NMR δ: 3.85 (td, CH_2, $^5J_{HF} = 2.0$ Hz); and 0.94 (q, CH_3) ppm. ^{19}F NMR δ: −37.7 (ddd, F-4, $^3J_{3-4} = 21.4$, $^3J_{4-5} = 20.3$, $^4J_{4-6} = 9.6$ Hz); −73.2 (broad t, F-3); −73.7 (ddt, F-5, $^4J_{3-5} = 5.4$, $^3J_{5-6} = 5.6$ Hz); and −75.5 (ddt, F-6, $^5J_{3-6} = 3.1$ Hz) ppm, parameters similar to those reported for other polyfluorocyclohexa-2,5-dienones [13]. IR ν_{max} (cm^{-1}): 1745; 1710 (C=C str.); and 1680 (C=O str.). Mass spectrum *m/z* (>10%): 228 (29.3%, M^+); 200 (87.2%, $C_7H_5F_5O^+$); 181 (15.2%, $C_7H_5F_4O^+$); 172 (46.8%, $C_6H_5F_5^+$); 152 (100.0%, $C_5F_4O^+$); 133 (11.4%, $C_5F_3O^+$); 124 (39.6, $C_4F_4^+$); 105 (11.6%, $C_4F_3^+$); and 45 (26.7%, $C_2H_5O^+$).

(h) Photolysis

The title heptene (0.220 g, 1.1 mmol) and dry nitrogen (260 mmHg), contained in a 1 l Hanovia photochemical reactor fitted with a silica insert, was irradiated for 14.5 h with light from a Hanovia low-pressure mercury lamp while nitrogen was passed through the insert. The volatile material then comprised the unchanged heptene (0.158 g, 0.76 mmol, 72% recovery), with an unidentified involatile material (60 mg) remaining in the reactor.

(i) Static pyrolysis

The title heptene (0.351 g, 1.74 mmol) was sealed *in vacuo* in an NMR tube and heated at 50 °C for 7 d when no starting material remained. Material which was volatile at room temperature was removed and identified as hexafluorocyclohexa-2,4-dienone (**6**) (0.210 g, 1.04 mmol, 60%) (Analysis: Found: C, 36.0: F, 56.2%. C_6F_6O requires: C, 35.7, F, 56.4%) as a pale yellow liquid. ^{19}F NMR (neat liquid) δ: −35.9 (dddd, F-6, $^3J_{5-6} = 22.2$, $^4J_{4-6} = 13.3$, $^4J_{2-6} = 7.5$, $^5J_{3-6} = 4.0$ Hz); −55.4 (tdd, F-3, $^3J_{2-3} = 2.1$, $^3J_{3-4} = 1.0$ Hz); −77.3 (tdd, F-5, $^5J_{2-5} = 20.9$, $^3J_{4-5} = 1.0$ Hz); −78.3 (tdt, F-4, $^4J_{2-4} = 4.3$ Hz); and −84.9 (F-2) ppm, parameters similar to those reported for other polyfluorocyclohexa-2,4-dienones [14]. IR ν_{max} (cm^{-1}): 1735 (C=C str.); and 1669 (C=O str.). Mass spectrum *m/z* (≥10%): 202 (66.1%, M^+); 174 (54.6%, $C_5F_6^+$); 155 (37.9%, $C_5F_5^+$); 124 (100.0, $C_4F_4^+$); 105 (17.5% $C_4F_3^+$); 93 (31.0%, $C_3F_3^+$); 74 (16.6, $C_3F_2^+$); 69 (35.9, CF_3^+); 31 (15.5%, CF^+); and 28 (54.0, CO^+).

Unidentified involatile material (0.140 g) remained in the tube.

(j) Flow pyrolysis

The vapour of the title heptene (0.525 g, 2.60 mmol) at 0.005 mmHg was passed through a silica tube (600×10 mm i.d., heated volume 40 cm^3) at 275 °C over 60 s (contact time *c.* 0.5 μs). The pyrolysate which collected in the first of two traps cooled to −78 °C and −196 °C was immediately examined by ^{19}F NMR spectroscopy, and this indicated the presence of five major components in the ratio 72:12:7:3:2 and traces (<3%) of unidentified carboxylic acid fluorides. The major component was hexafluorocyclohexa-2,4-dienone (**6**) and the remaining components were identified spectroscopically as pentafluorocyclopenta-1,3-diene 1-carboxylic acid fluoride (**8**), pentafluorocyclopenta-1,3-diene 5-carboxylic acid fluoride (**7**), 1,2-difluorofumaryl fluoride and 1,2-difluoromaleyl fluoride, respectively. Only the cyclohexadienone **6** (70%) was obtained from an attempted GLC separation (2 m SE30 on Celite at 50 °C), the acid fluorides being retained on the column.

The pentafluorocyclopenta-1,3-diene 1-carboxylic acid fluoride (**8**) showed the following ^{19}F NMR parameters δ: 109.9 (ddt, COF, $^4J_{1-2}=36.3$, $^5J_{1-4}=8.8$, $^4J_{1-5}=2.7$ Hz); −16.6 (dqd, F-2, $^3J_{2-3}=8.1$, $^4J_{2-4}=3.2$, $^4J_{2-5}=8.3$ Hz); −57.5 (dddd, F-5, $^4J_{3-5}=5.5$, $^3J_{4-5}=9.1$ Hz); −70.9 (dqd, F-4, $^3J_{3-4}=12.6$ Hz); and ~ −78.5 (F-3, partly masked by an absorption of the major component) ppm. These should be compared with the parameters reported for 1-cyano- [15] and 1-trifluoromethyl-pentafluorocyclopenta-1,3-diene [16]. The cyano compound, in particular, shows the expected similarities with δ −28.0 (F-2), −54.6 (F-5), −73.0 (F-4) and −76.0 ppm (F-3), and $^3J_{2-3}=9.0$, $^4J_{2-4}=2.0$, $^4J_{2-5}=8.3$, $^3J_{3-4}=14.2$, $^4J_{3-5}=5.5$ and $^3J_{4-5}=8.6$ Hz.

The pentafluorocyclopenta-1,3-diene 5-carboxylic acid fluoride (**7**) showed the following ^{19}F NMR parameters δ: 95.4 (d, COF-6, $^3J_{5-6}=19.3$ Hz); −71.5 (F-2,3); −88.6 (F-1,4); and −117.6 (dtt, F-5, $^3J_{1-5}=16.2$, $^4J_{2-5}=3.6$ Hz) ppm. The −71.5 and −88.6 ppm absorptions comprised an aa'xx' subspectrum, but the spectral intensity was insufficient for the extraction of coupling constants. For comparison, 5-chloropentafluorocyclopenta-1,3-diene shows δ −68.2 (F-5), −80.7 (F-2,3) and −92.2 (F-1,4) ppm [17], and in the 5-COF compound the high- and low-field absorptions are characteristic of a fluorine atom attached to a tertiary carbon atom and a COF group, respectively.

Two AA'XX'-type spectra were weakly apparent in the spectrum of the mixture, with absorptions at δ 103.7 and −73.7, and 105.3 and −51.0 ppm. These were tentatively assigned to difluorofumaryl and difluoromaleyl fluoride, respectively, by comparison with the chemical shift data for perfluorobut-2-enoyl fluoride: *trans* isomer δ 104.4 (COF); −68.4 (F-3); and −80.4 (F-2) ppm; and *cis* isomer δ: 104.8 (COF); −51.0 (F-3); and −64.3 (F-2) ppm [18].

(k) Miscellaneous reactions

The title heptene was shaken with caesium fluoride in sulpholane at room temperature for 2 h, but no volatile product was obtained. When

warmed from −196 °C to room temperature with anhydrous aluminium chloride, it exploded violently. With aluminium chloride in methylene chloride at −10 °C for 1 h, two products appeared (GLC) to be formed but they decomposed rapidly. Only high molecular weight material was obtained with triethylamine in tetrahydrofuran at −78 °C for 2 h with subsequent warming to room temperature.

Flow pyrolysis of the adducts of hexafluoro-3-oxatricyclo[3.2.0.0^{2,4}]-hept-6-ene

(a) Benzonitrile oxide adduct

The benzonitrile adduct **14** (0.231 g, 0.72 mmol), heated to 65 °C and passed at 0.005 mmHg through a silica tube (heated volume 40 cm^3) heated to 440 °C during 20 min (contact time 8 ms), gave a pyrolysate (0.231 g, 100%) which was sublimed at 70 °C/0.005 mmHg leaving unidentified involatile material (63 mg), and recrystallised from n-pentane to give 1,2,3,5,6,7-hexafluoro-8-phenyl-4,10-dioxa-9-azabicyclo[5.3.0]deca-2,5,8-triene (**21**) (nc) (0.120 g, 0.37 mmol, 52%) (Analysis: Found: C, 48.9; H, 1.4; F, 35.5; N, 4.6%; mol. wt., 321. $C_{13}H_5F_6NO_2$ requires: C, 48.6; H, 1.6; F, 35.5; N, 4.4%; mol. wt., 321) as a white solid (m.p., 68–70 °C). ^{19}F NMR (30% w/v in $CDCl_3$) δ: −7.3 (ddt, F-5, $^3J_{5-6}=27.5$, $^4J_{5-7}=6.9$, $^5J_{2-5}=^4J_{3-5}=4.4$ Hz); −16.7 (ddt, F-3, $^3J_{2-3}=23.0$, $^4J_{1-3}=9.0$, $^5J_{3-6}=4.4$ Hz); −30.9 (dddd, F-1, $^3J_{1-2}=25.9$, $^3J_{1-7}=13.5$, $^4J_{1-6}=2.0$ Hz); −83.5 (broad ddd, F-6, $^3J_{6-7}=20.9$ Hz); −85.7 (ddt, F-3); and −100.0 (ddd, F-2) ppm. This assignment was made on the assumption that the CF−O absorptions occur to low-field, the pairs of fluorines, F-3 and F-5, F-2 and F-6, and to a lesser extent F-1 and F-7, should show similar parameters, and the long-range coupling constants should have the smallest magnitude. The CF−O fluorines in **25** occur at −18.3 ppm (converted from $CFCl_3$ reference) [19]. IR ν_{max} (cm^{-1}): 1779; and 1761 (C=C str.). Mass spectrum *m/z* (>10%): 321 (38.8%, M^+); 202 (10.5%, $C_6F_6O^+$); 180 (12.8%, $C_{10}H_3F_3^+$); 174 (15.2%, $C_{11}H_4F_2^+$); 171 (10.7%, $C_5F_5O^+$); 124 (14.1%, $C_4F_4^+$); 119 (60.5, $C_7H_5NO^+$); 103 (100.0%, $C_7H_5N^+$); 93 (14.9%, $C_3F_3^+$); 91 (17.2%, $C_6H_5N^+$); 77 (33.1, $C_6H_5^+$); 76 (27.3%, $C_6H_4^+$); 64 (12.7%, $C_5H_4^+$); 51 (19.7%, $C_4H_3^+$); 50 (10.2%, $C_4H_2^+$, CF_2^+).

When the benzonitrile adduct, heated to 80 °C, was passed at 400 °C/3.5 mmHg through the silica tube with a much longer contact time (*c.* 42 s), it yielded hexafluorocyclohexa-2,4-dienone (55%), benzonitrile (18%), 3,4-diphenylfuroxan (51%) and a tar.

(b) The dichloride

When the vapour of 6,7-dichlorohexafluoro-3-oxatricyclo[3.2.0.0^{2,4}]-heptane (**18a** and **19a**) (0.380 g, 1.4 mmol) was passed through the same silica tube at 415 °C/0.005 mmHg over 10 min (contact time *c.* 2 ms), it gave unidentified polymeric material (54 mg) and a fraction which condensed *in vacuo* at −78 °C, which was separated by GLC methods (4 m SE30 on Celite at 80 °C) to give a 2.5:1 mixture of *cis*- and *trans*-4,5-dichloro-

2,3,4,5,6,7-hexafluoro-5,6-dihydro-oxepin (**20**) (0.185 g, 0.93 mmol, 66%) (Analysis: Found: C, 26.6; F, 40.3%; mol. wt., 272. $C_6Cl_2F_6O$ requires: C, 26.4; F, 41.8%; mol. wt., 272), and an unidentified isomeric (by mass spectrometry, *m/z*: 272, M^+) compound (51 mg, 13%). The dihydro-oxepin **20** showed the following ^{19}F NMR (40% in $CDCl_3$) characteristics δ: sets of overlapping absorptions at *c.* −19 (F-2,7); −34 (F-4,5); and −88 (F-3,6) ppm.

(c) The dibromide

The vapour of 6,7-dibromohexafluoro-3-oxatricyclo[3.2.0.$0^{2,4}$]heptane (**18b** and **19b**) (0.355 g, 1.0 mmol), passed through the same silica tube at 425 °C/0.005 mmHg over 10 min (contact time *c.* 3 ms), gave a pyrolysate (0.349 g) from which bromine was removed by shaking with mercury, and the remainder (0.20 g) was shown by GLC methods (2 m SE30 on Celite at 50 °C, programmed to 200 °C) to contain at least 30 components; it was not examined further.

*Attempted dechlorination of 4,5-dichlorohexafluoro-4,5-dihydro-oxepin (**20**)*

Passage of the vapour of the title compound over copper-bronze at 165 °C and 245 °C led only to recovered starting material (70%). Attempts on a small scale to effect dechlorination in tetrahydrofuran with the following reagents: (i) activated zinc at room temperature for 18 h; (ii) magnesium at room temperature for 18 h; (ii) zinc–copper couple at room temperature; and (iv) sodium naphthalene anion–radical at −24 °C for 1 h, yielded no material of the volatility expected for C_6F_6O, as indicated by GLC methods.

Reaction of hexafluoro[2.2.0]hexa-2,5-diene with benzonitrile oxide

Phenylhydroxamic acid chloride (5.4 g, 35 mmol) was added in portions over 15 min to a well-stirred mixture of aqueous sodium hydroxide (0.1 M, 20 cm^3) and diethyl ether (20 cm^3) at 0 °C. The ethereal solution was then separated, dried at 0 °C ($MgSO_4$) and added to a magnetically-stirred solution of hexafluorobicyclo[2.2.0]hexa-2,5-diene (**1**) (6.6 g, 35 mmol) in diethyl ether (15 cm^3) containing $MgSO_4$ (1 g) which was kept at 0 °C overnight. The volatile material was then removed *in vacuo* and unreacted diene estimated by GLC methods. A further equivalent of benzonitrile oxide was then added, and this process was repeated until no diene remained.

The combined solid residues were sublimed at 55 °C/0.01 mmHg to give 1,2,3,4,5,6-hexafluoro-7-phenyl-9-oxa-8-azatricyclo[4.3.0.$0^{2,5}$]nona-3,7-diene (**15**) (nc) (7.0 g, 23 mmol, 65%) (Analysis: Found: C, 51.0; H, 1.4; F, 37.7; N, 4.5%; mol. wt. 305. $C_{13}H_5F_6NO$ requires: C, 51.2; H, 1.6; F, 37.4; N, 4.6%; mol. wt. 305) as a white solid (m.p., 62 °C). ^{19}F NMR ($CDCl_3$) δ: −41.1 (2F, F-1 and F-3 or -4); −45.9 (F-3 or -4); −85.0 (F-6); −107.0 and 112.5 (F-2 and F-5). IR ν_{max} (cm^{-1}): 1750 (CF=CF str.)

Fractional crystallisation from ethanol of the soluble residue gave, in order of increasing solubility, 3,4-diphenylfuroxan (0.50 g, 2.1 mmol),

1,2,6,7,8,12-hexafluoro-3,9-diphenyl-5,11-dioxa-4,10-diazatetracyclo[5.5.0.0.^{2,6}0^{8,12}]dodeca-3,9-diene (**17**) (nc) (1.4 g, 3.3 mmol, 14%) (Analysis: Found: C, 56.2; H, 2.2; N, 6.8%; mol. wt., 426. $C_{20}H_{10}F_6N_2O_2$ requires: C, 56.6; H, 2.4; N, 6.6% mol. wt., 426), as a white solid (m.p., 160 °C), and 1,2,6,7,8,12-hexafluoro-3,11-diphenyl-5,9-dioxa-4,10-diazatetracyclo-[5.5.0.0.^{2,6}0^{8,12}]dodeca-3,10-diene (**16**) (nc) (0.7 g, 1.6 mmol, 7%) (Analysis: Found: C, 56.5; H, 2.2; N, 6.8%; mol. wt., 426. $C_{20}H_{10}F_6N_2O_2$ requires: C, 56.6; H, 2.4; N, 6.6%; mol. wt., 426) as a white solid (m.p., 110 °C). The 3,9-diene showed ^{19}F NMR δ: −49.0 (F-6, 12); −96.8 (F-2, 8); and −101.6 (F-1, 7) ppm, and the 3,10-diene showed δ: −53.4 (F-6, 8); −92.6 (F-2, 12); and −96.1 and −107.1 (F-1 and F-7) ppm.

Pyrolysis of 1,2,3,4,5,6-hexafluoro-7-phenyl-9-oxa-8-azatricyclo-[4.3.0.0^{2,5}]nona-3,7-diene

(a) Static conditions

The title diene **15** (100 mg, 0.33 mmol), sealed *in vacuo* in a Pyrex ampoule (5 cm^3) and heated at 160 °C for 3 d, gave a pale yellow liquid which was purified by GLC methods (2 m SE30 column at 145 °C) to give 1,2,3,4,5,6-hexafluoro-7-phenyl-9-oxa-8-azabicyclo[4.3.0]nona-2,4,7-triene (**24**) (nc) (96 mg, 0.31 mmol, 96%) (Analysis: Found: C, 51.4: H, 1.6; F, 37.8; N, 4.8%; mol. wt. 305. $C_{13}H_5F_6NO$ requires: C, 51.2; H, 1.7; F, 37.4; N, 4.6%; mol. wt., 305) as a pale yellow liquid (b.p., 268 °C/760 mmHg). ^{19}F NMR δ: −54.1 (F-1); −70.4; −75.3 (F-3 and -4); −78.8; −80.0 (F-2 and -5); and −85.3 (F-6) ppm. IR ν_{max} (cm^{-1}): 1750 and 1695 (C=C) str.).

(b) Flow conditions

The title diene (0.30 g, 0.98 mmol) was heated to 60 °C and passed as the vapour at 0.005 mmHg through a silica tube (600 × 10 mm i.d., heated volume 40 cm^3) at 450 °C over 20 min (contact time *c.* 5 ms) to give the above triene **24** (0.28 g, 0.91 mmol, 93%).

The title diene (0.229 g, 0.75 mmol) was heated to 75 °C and passed at 3.5 mmHg through the same tube heated to 445 °C over 3.5 h (contact time *c.* 52 s) to give a product which was fractionated by trap-to-trap distillation *in vacuo* to give a mixture of hexafluorobenzene (67 mg, 0.36 mmol, 48%) and benzonitrile (1.5 mg, 15 mmol, 2%) which condensed at −78 °C, a mixture of 3,4-diphenylfuroxan (21 mg, 0.25 mmol, 33%) and a tar (40 mg) which condensed at 0 °C.

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References

1 (a) Part 12, M. G. Barlow, R. N. Haszeldine and C. J. Peck, *J. Fluorine Chem.*, *20* (1982) 771; (b) preliminary communication, M. G. Barlow, R. N. Haszeldine and C. J. Peck, *J. Chem. Soc., Chem. Commun.*, (1980) 158.
2 G. Cammaggi, F. Gozzo and G. Cevidalli, *Chem. Commun.*, (1966) 313; I. Haller, *J. Am. Chem. Soc.*, *88* (1966) 2070.
3 D. Sianesi, *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.*, *12* (1971) 411; D. Sianesi, A. Pasetti, R. Fontanelli, G. C. Bernardi and G. Caproriccio, *Chem. Ind. (Milan)*, *55* (1973) 208.
4 E. Vogel, R. Schubard and W. A. Boll, *Angew. Chem., Int. Ed. Engl.*, *3* (1964) 510; E. Vogel, W. A. Boll and H. Günther, *Tetrahedron Lett.*, (1965) 609.
5 H. Günther, *Tetrahedron Lett.*, (1965) 4085.
6 N. E. Takenaka, R. Hamlin and D. M. Lemal, *J. Am. Chem. Soc.*, *112* (1990) 6715.
7 M. G. Barlow, R. N. Haszeldine and R. Hubbard, *J. Chem. Soc. C*, (1971) 90.
8 M. G. Barlow, R. N. Haszeldine, W. D. Morton and D. R. Woodward, *J. Chem. Soc., Perkin Trans. 1*, (1973) 1798.
9 M. G. Barlow, G. M. Harrison, R. N. Haszeldine, R. Hubbard, M. J. Kershaw and D. R. Woodward, *J. Chem. Soc., Perkin Trans. 1*, (1975) 2010.
10 M. G. Barlow, R. N. Haszeldine, W. D. Morton and D. R. Woodward, *J. Chem. Soc., Perkin Trans. 1*, (1972) 2170.
11 M. G. Barlow, G. M. Harrison, R. N. Haszeldine, W. D. Morton, P. Shaw-Luckman and M. D. Ward, *J. Chem. Soc., Perkin Trans. 1*, (1982) 2101.
12 A. H. Nielsen, T. G. Burke, P. J. Woltz and E. A. Jones, *J. Chem. Phys.*, *20* (1952) 596.
13 N. G. Kostina and V. D. Shteingarts, *Zh. Org. Khim.*, *9* (1973) 569.
14 N. E. Akhmetova, N. V. Kostina, V. J. Mamatyuk, A. A. Shtark and V. D. Shteingarts, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, (1973) 86 [*Chem. Abs.*, *80* (1974) 107 493s].
15 B. Al-Saleh, R. E. Banks, M. G. Barlow and J. C. Hornby, *J. Fluorine Chem.*, *12* (1978) 341.
16 G. Camaggi and F. Gozzo, *J. Chem. Soc. C*, (1971) 925.
17 R. E. Banks, M. Bridge, R. N. Haszeldine, D. W. Roberts and N. I. Tucker, *J. Chem. Soc. C*, (1970) 2531.
18 R. E. Banks, M. G. Barlow and K. Mullen, *J. Chem. Soc. C*, (1969) 1331.
19 M. S. Toy and R. S. Stringham, *J. Org. Chem.*, *44* (1979) 2813; M. S. Toy and R. S. Stringham, *J. Fluorine Chem.*, *12* (1978) 23.