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# 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

Michael G. Barlow** and Colin J. Peck

*Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD (UK)*

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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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**Author to whom correspondence should be addressed.

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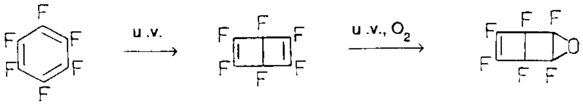
isomerisation of the benzene to its isomer, Dewar benzene (**1**), and much more slowly to the formation of the Dewar-benzene oxide (**2**), the yield being about 10% after 75 h irradiation (Scheme 1). Much oxygen-containing, polymeric material was also formed, and this tended to coat the silica insert 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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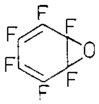
Scheme 1.



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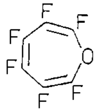

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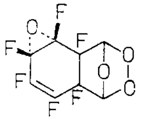

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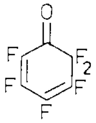

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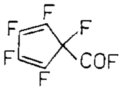

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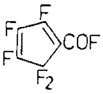

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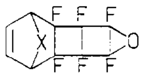
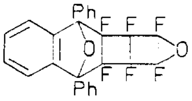


(**11**; X = $CH_2$)

(**12**; X = O)



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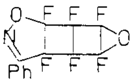

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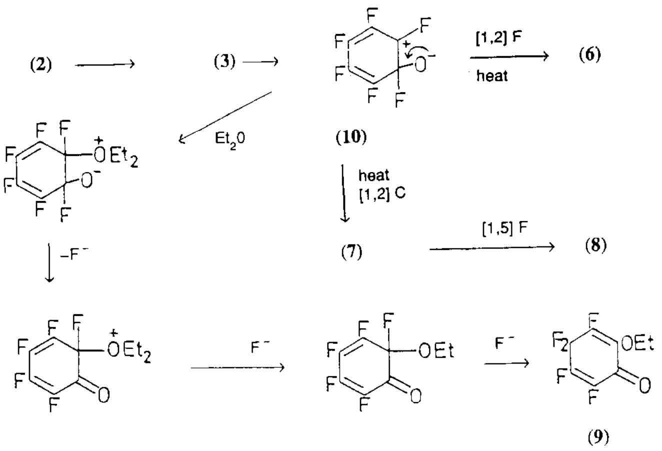
of **1** in the presence of oxygen resulted in a more rapid formation of the oxide **2**.

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].

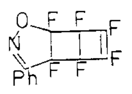
The oxide **2** when heated at 50 °C for 7 d gave the dienone **6** (60%) as the only volatile product. Flow pyrolysis at 275 °C in silica with a short (0.5 $\mu$s) contact time yielded the dienone **6** (72%), together with the isomeric acid fluorides **7** (12%) and **8** (7%) (identified spectroscopically) 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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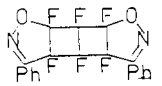

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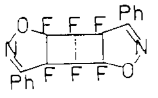

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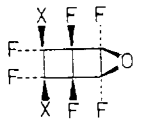
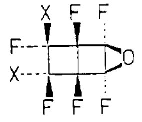


(18a, X = Cl; b, X = Br)



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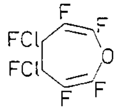

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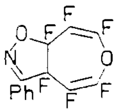

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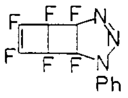
that the benzene oxide **3** is reduced under very mild conditions to pentafluorophenol [6], so our failure is not surprising.

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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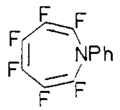

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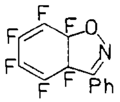

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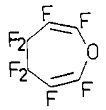

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In the hexafluorobenzene oxide–hexafluoro-oxepin system, the equilibrium strongly favours the benzene oxide [6], which contrasts with the case of azepines such as **23**, where no bicyclic isomer was detected [11]. Our failure to obtain the benzene 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) $\delta$: −43.3 (F-6 and -7); −97.0 (F-2 and -4); and −119.0 (F-1 and -5) ppm. IR $\nu_{max}$ ($cm^{-1}$): 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). $^1H$ NMR (30% in $CDCl_3$) $\delta$: 6.52 (H-10 and -11); 3.43 (H-1 and -9); and 1.65 (H-12) ppm. $^{19}F$ NMR $\delta$: −96.4; −98.4; and −116.7 (all 2F) ppm. IR $\nu_{max}$ (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). $^1H$ NMR (30% w/v $CDCl_3$) $\delta$: 6.75 (H-10 and -11); and 5.28 (H-1 and -9) ppm. $^{19}F$ NMR $\delta$: −103.1; −105.2; and −118.0 (all 2F) ppm. IR $\nu_{max}$ (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 $Et_2O$) $\delta$: −98.0; 108.0; and −119.5 (all 2F) ppm. IR $\nu_{max}$ (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-azatetracyclo[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 $CDCl_3$) $\delta$: $-45.0$ (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 $\nu_{max}$ (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 $CCl_4$) $\delta$: *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 $\nu_{max}$ (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 $CCl_4$) $\delta$: $-36.0$ (F-6 and -7); $-95.7$ (F-2 and -3); and $-98.7$ (F-1 and -5) ppm. IR $\nu_{max}$ (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. $^1$H NMR $\delta$: 3.85 (td, $CH_2$, $^5J_{HF} = 2.0$ Hz); and 0.94 (q, $CH_3$) ppm. $^{19}$F NMR $\delta$: −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 $\nu_{max}$ (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) $\delta$: −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 $\nu_{max}$ (cm$^{-1}$): 1735 (C=C str.); and 1669 (C=O str.). Mass spectrum *m/z* ($\geqslant$ 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 $\mu$s). 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 $\delta$: 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 $\delta$ −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 $\delta$: 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 $\delta$ −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 $\delta$ 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 $\delta$ 104.4 (COF); −68.4 (F-3); and −80.4 (F-2) ppm; and *cis* isomer $\delta$: 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 $CDCl_3$) $\delta$: −7.3 (ddt, F-5, $^3J_{5\text{–}6} = 27.5$, $^4J_{5\text{–}7} = 6.9$, $^5J_{2\text{–}5} = {}^4J_{3\text{–}5} = 4.4$ Hz); −16.7 (ddt, F-3, $^3J_{2\text{–}3} = 23.0$, $^4J_{1\text{–}3} = 9.0$, $^5J_{3\text{–}6} = 4.4$ Hz); −30.9 (dddd, F-1, $^3J_{1\text{–}2} = 25.9$, $^3J_{1\text{–}7} = 13.5$, $^4J_{1\text{–}6} = 2.0$ Hz); −83.5 (broad ddd, F-6, $^3J_{6\text{–}7} = 20.9$ 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 $\nu_{max}$ (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 $\delta$: 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 ($CDCl_3$) $\delta$: −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 $\nu_{max}$ (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 $\delta$: −49.0 (F-6, 12); −96.8 (F-2, 8); and −101.6 (F-1, 7) ppm, and the 3,10-diene showed $\delta$: −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 $\delta$: −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 $\nu_{max}$ (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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