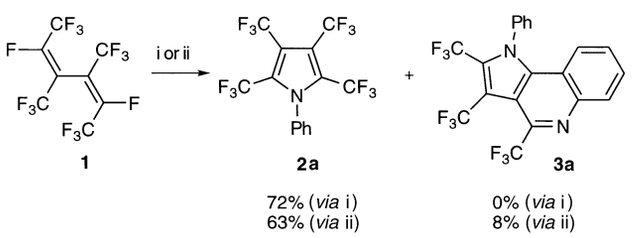
Reactions involving fluoride ion. Part 42.[1] Heterocyclic compounds from perfluoro-3,4-dimethylhexa-2,4-diene

Richard D. Chambers,*[,a] William K. Gray,[a] Steven J. Mullins[a] and Stewart R. Korn[b]

[a] *Department of Chemistry, University of Durham, Science Laboratories, South Road, Durham, UK DH1 3LE*
[b] *Zeneca Specialties, Leeds Road, Huddersfield, UK HD2 1FF*

Reactions of perfluoro-3,4-dimethylhexa-2,4-diene 1 with primary aromatic amines give both pyrrole 2 and pyrroloquinoline 3 derivatives, whilst ammonia gives dienes 10 and 12 as well as the novel pyrrole derivative 11. Catechol leads to a benzodioxocine system 18 and this can be epoxidised to a mixture of mono- 21 and di-epoxides 20. Electrocyclisation of 18 occurs with ultraviolet irradiation, giving 22.

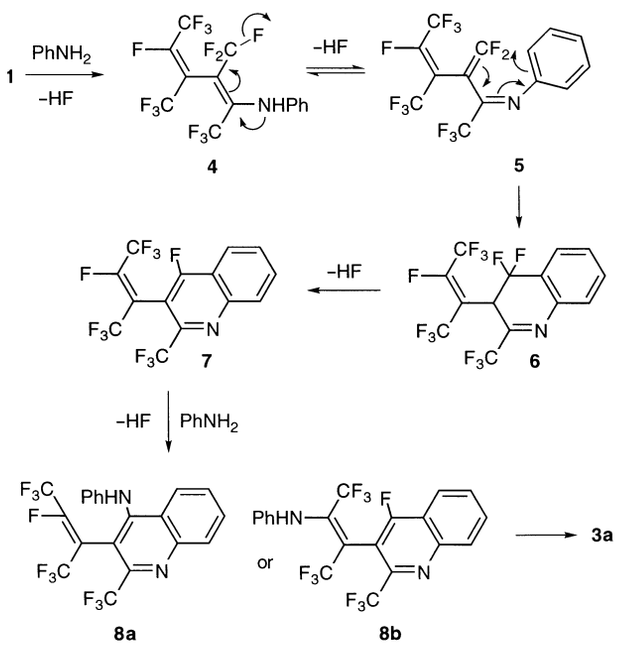
We have recently described[2,3] a simple preparation of perfluoro-3,4-dimethylhexa-2,4-diene **1** from an oligomer of tetrafluoroethene[4,5] and this diene has proved to be a very reactive difunctional electrophile. Direct formation of cyclic systems occurs readily and we have already described the formation of furan, thiophene,[2,3] cyclopentadiene and cyclopentadienide derivatives.[1] Here we describe further reactions that lead to novel heterocycles.



Scheme 1 *Reagents and conditions:* i, $PhNH_2$, CsF, CH_3CN, room temp.; ii, $PhNH_2$, KF, CH_3CN, room temp.

Reaction of aniline with the diene **1** gave the anticipated pyrrole derivative **2a** but, remarkably, this was accompanied by the formation of the novel pyrroloquinoline derivative **3a** (Scheme 1). The structure of the pyrrole derivative **2a** followed simply from the NMR data which, for example, showed two resonances at δ_F −54.3 and −54.7, associated with trifluoromethyl groups, in the ^{19}F NMR spectrum. However, it was much more difficult to elucidate the structure of **3a**, and this was deduced initially from a consideration of mechanism. The process is shown in Scheme 2, where initial displacement of vinylic fluorine occurs, giving the amine **4**, and then displacement of fluoride ion from this amine leads to **5**, which is ideally arranged for electrocyclisation to form the quinoline nucleus, after further loss of hydrogen fluoride from **6**, giving **7**. The quinoline system **7** has a fluorine substituent on the 4-position that is highly activated towards nucleophilic displacement because not only the ring nitrogen but also the fluorocarbon groups will be activating. Therefore, further reaction with aniline could occur to give **8a**. However, intermediate **7** also has a vinylic fluorine atom that is very reactive towards aniline and the process leading to **8b** is one which we cannot exclude. However, either of these intermediates, *i.e.* **8a** or **8b**, would then lead to the product **3a**, by electrocyclisation and subsequent loss of hydrogen fluoride.

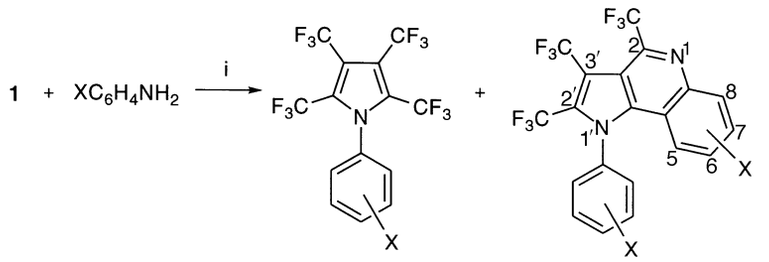
Clearly, the crucial step in formation of the pyrroloquinoline derivative **3a** is loss of fluoride ion from intermediate **4** and we



Scheme 2

attempted to suppress this step by adding excess fluoride ion to the system. Potassium fluoride had little influence on product ratios but is useful in removing hydrogen fluoride from the system, whereas the more reactive caesium fluoride led to exclusive formation of **2a**. Spectral data are entirely consistent with the proposed structure of **3a**; mass spectrometry gave the molecular ion and the ^{19}F NMR spectrum showed three resonances for trifluoromethyl groups and two, at δ_F −51.6 and −52.9, are in the same region as for the pyrrole derivative **2a**, while the presence of a phenylpyrrole is consistent with the multiplet centred at δ_H 7.8 in the ^1H NMR spectrum, also comparable to **2a**. The ^1H NMR spectrum also showed resonances, at δ_H 6.83, 7.47, 7.80 and 8.27, that are reasonably assigned to the benzenoid ring of **3a** by comparison with the spectrum of quinoline, which shows resonances at δ_H 7.41, 7.60, 7.70 and 8.09 for ring protons in similar positions.

We also investigated the product distribution, corresponding to **2a** and **3a**, starting with substituted anilines (Scheme 3), reasoning that systems with electron-withdrawing groups would have a reduced tendency for expulsion of fluoride ion



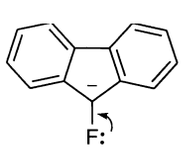
Scheme 3 *Reagents and conditions:* i, KF, CH_3CN, room temp.

Table 1 Reaction of **1** and subsitiuted anilines $XC_6H_4NH_2$ to give **2** and **3**[a]

X	Pyrrole **2** (% yield)	Pyrroloquinoline **3** (% yield)
p-H	**2a** (67)	**3a** (27)
p-NMe_2	**2b** (81)	—
p-OMe	**2c** (73)	**3c** (21)
o-OMe	**2d** (37)	**3d** (37)
m-OMe	**2e** (50)	**3e** (19)[b]
p-F	**2f** (45)	**3f** (52)
p-Cl	**2g** (18)	*c*
p-NO_2	**2h** (79)	—

[a] All yields listed are crude yields based on ^{19}F NMR spectroscopic integration of trifluoromethyl resonances against trifluorotoluene as a marker. [b] Combined yield of products (see Experimental section). [c] The reaction with 4-chloroaniline gave a complex mixture of products and the presence of the pyrroloquinoline derivative could not be unequivocally established.

from intermediate **4** and hence a lower proportion of analogues of **3a** in the product. Conversely, systems with electron-donating groups would increase the proportion of these products. Results are shown in Table 1, with some surprising observations. A *para*-nitro group clearly eliminates the formation of **3** but, remarkably, the same result was observed for the *para*-dimethylamino derivative, which should be a good donor! However, hydrogen fluoride is released in the reaction and it seems reasonable to conclude, therefore, that the dimethylamino group is protonated and therefore rendered electron-withdrawing, hence suppressing formation of **3**. The analogous argument could be applied for the position of the *para*-methoxy derivative in Table 1 and the other surprising result is that a fluorine substituent is effective in *promoting* formation of **3**. This is a further illustration of π-inductive repulsion between non-bonding electron pairs on fluorine and π-electron-rich systems. For example, it is known that a *para*-fluorine substituent at the carbanion site in the 9-fluorofluorenyl anion **9** is destabil-



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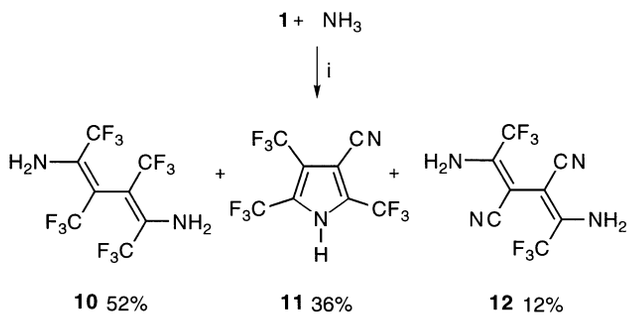
ising, with respect to the parent anion,[6] and that *para*-fluorine substituents are slightly deactivating with respect to nucleophilic aromatic substitution.[7]

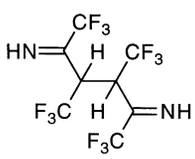
Consistent with these observations is the fact that *ortho*-methoxyaniline gave a slightly increased proportion of the corresponding pyrroloquinoline derivatives over the *para*-isomer, whereas *meta*-methoxyaniline gave only a small proportion of **3e**, in a slow reaction.

Reaction of **1** with ammonia gave products arising from a relatively complex process (Scheme 4). The diene **10** arose from simple vinylic displacement of fluorine but diene **12** and the



Scheme 4 *Reagents and conditions:* i, KF, THF, room temp.

pyrrole derivative **11** contain nitrile groups, arising from loss of fluorine from trifluoromethyl, which is analogous to the loss of fluoride from intermediate **4** in Scheme 2. The diamines **10** and **12** exist in the amine form and no evidence could be found for imine forms *e.g.* **13**, and this is especially significant because



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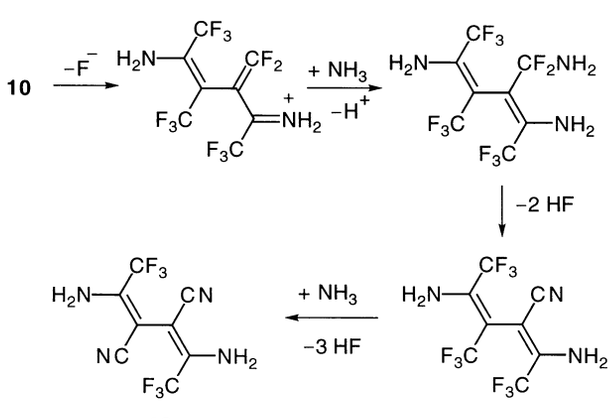
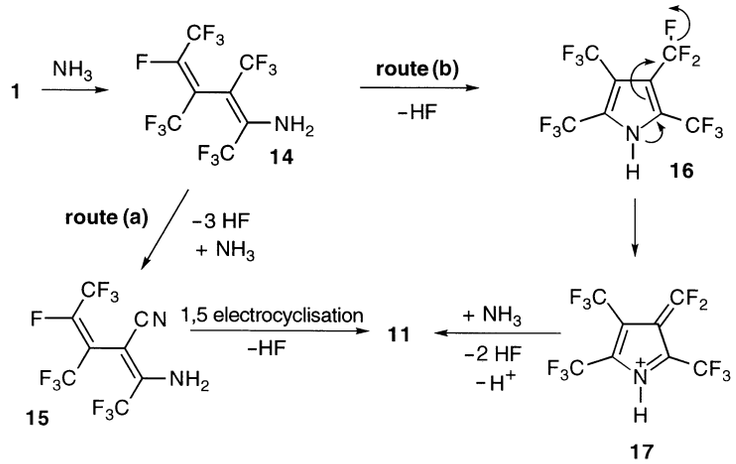
analogous hydrocarbon derivatives are observed almost exclusively in the diimino forms.[8] It is well established that perfluoroalkyl groups lower π-orbital energies[9] and it is possible that preference of the fluorocarbon system **10** for the diamine structure arises from the fact that, in that form, all of the trifluoromethyl groups are directly attached to the π-system and therefore maximise their stabilising influence. A process for the formation of **12** is outlined in Scheme 5.



Scheme 5

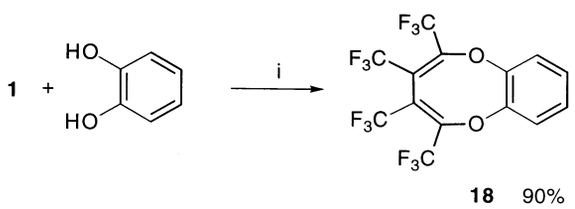
Formation of the pyrrole derivative **11** could be accounted for by either of routes (a) or (b) in Scheme 6. However, it is not



Scheme 6

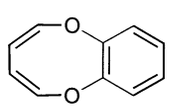
clear why loss of fluorine from a second trifluoromethyl should not occur from **11**, if loss of fluorine from the intermediate pyrrole **14** occurs. Therefore, the route (a) seems more likely. This process would involve an interconversion of dienes **14** and **15** which becomes easy after the introduction of an amino group, followed by electrocyclisation and loss of hydrogen fluoride.

Reaction of **1** with catechol gave the novel dioxocine derivative **18** (Scheme 7) and the structure followed simply from the



Scheme 7 *Reagents and conditions:* i, CsF, CH_3CN, 7 days, room temp.

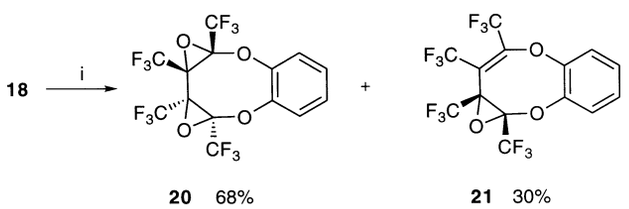
^{19}F NMR spectrum, which showed two resonances at positions very similar to those of the starting diene **1**. Earlier work on the dioxocine system **19**,[12–14] which is formally a 10π ring, has not



revealed any evidence for aromaticity and we have formed the same conclusion for trifluoromethylated systems. Although the benzodioxocine ring system **18** has 10π electrons, and as such conforms to the Hückel rules, the absence of a significant bathochromic shift in its ultraviolet spectrum (λ_{max} = 229 and 273 nm) when compared with catechol (λ_{max} = 214 and 278 nm)[10] suggests that the dioxocine ring is not involved in extending the aromaticity of the molecule. Further, theoretical studies of the parent hydrocarbon **19**[11–14] suggested that such systems are non-planar and, thus, non-aromatic.

In accordance with the proposed diene character of **18** it readily reacts with hypochlorite to give a mixture of di- and mono-epoxides **20** and **21** (Scheme 8), *i.e. via* a nucleophilic epoxidation process.

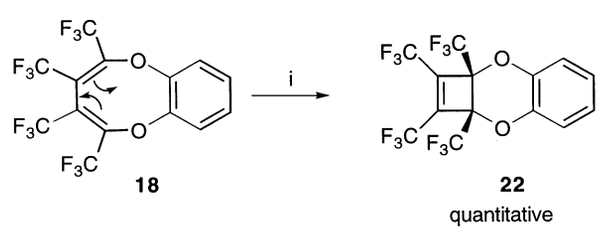
The ^{13}C NMR spectra of the two products clearly revealed the formation of epoxides because resonances associated with the alkenic carbon atoms in **18** at δ_C 107.5 and 144.4 were replaced with resonances associated with saturated sites in the product, *e.g.* in **20** with a dramatic upfield shift to δ_C 63.7 and 82.8. The epoxidation reaction was remarkably clean, giving



Scheme 8 *Reagents and conditions:* i, $Ca(OCl)_2$, CH_3CN, 4 days, 80 °C

only one detectable stereoisomer of **20**, as indicated by GLC–MS and the relative simplicity of the various NMR data, *e.g.* the ^{19}F NMR spectrum showed only two trifluoromethyl resonances at δ_F −65.3 and −69.1. These data indicate a symmetrical system but we are unable to distinguish between diastereoisomer **20** and the corresponding isomer which would be obtained by delivery of both oxygen atoms to the same face of compound **18**. Nevertheless, we have assigned the isomer as structure **20** because it seems highly probable that avoidance of eclipsing interactions by adjacent trifluoromethyl groups is the basis of the stereospecificity in the epoxidation reaction.

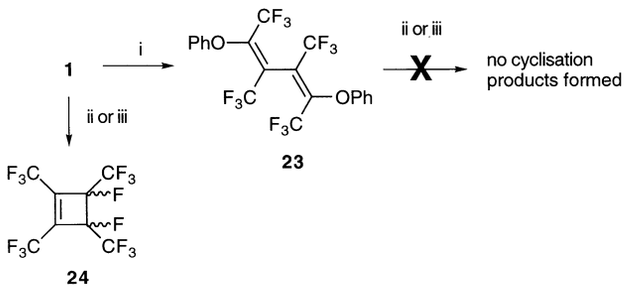
Further indication of the diene character of **18** is provided by the efficient [2 + 2] electrocyclisation, giving **22**, that occurs under irradiation from a medium pressure mercury lamp (Scheme 9). The stereochemistry of **22**, with the two trifluoro-



Scheme 9 *Reagents and conditions:* i, *hν*, CH_3CN, 24 h

methyl groups *cis* to one another, is as predicted by the Woodward–Hofmann rules. A *cis* arrangement for the trifluoromethyl groups is confirmed by the simplicity of the ^{19}F NMR spectrum of **22**, which shows only two CF_3 resonances, indicating that the molecule is symmetrical. Compound **18** decomposes at 180 °C, before any thermal electrocyclisation occurs.

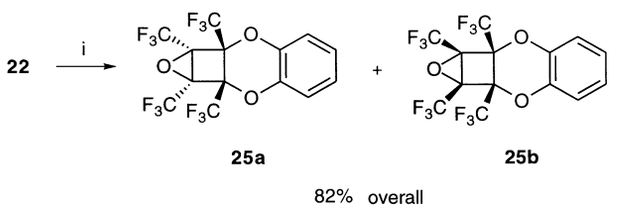
It has been previously established that diene **1** will cyclise both photochemically and thermally to **24** (Scheme 10). For comparison, therefore, we have made the diphenoxy compound **23**, which is electronically equivalent to **18**, by reaction of **1** with phenol.[15,16] In contrast cyclisation did not occur, either thermally of photochemically, and it can be concluded, therefore, that the presence of more sterically demanding



Scheme 10 *Reagents and conditions:* i, CsF, PhOH, 48 h, room temp.; ii, *hv*, CH_3CN, 24 h; iii, 80 °C, CH_3CN, 48 h

substituents than the vinylic fluorine atoms on **1** hinders the process by making the intermediate *cisoid* conformation less likely to form.

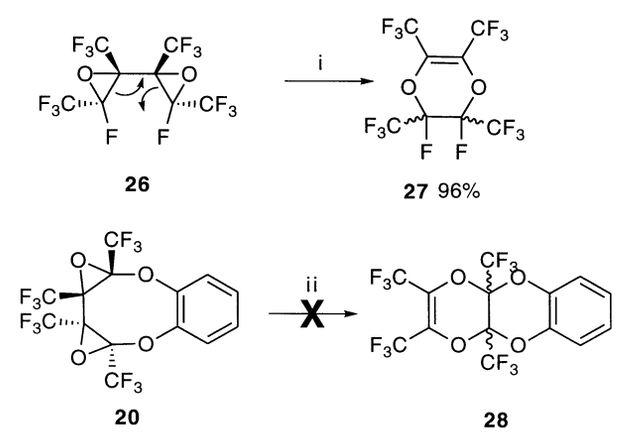
The tricyclic system **22** can also be epoxidised in high yield (Scheme 11). The ^{19}F NMR spectrum revealed the presence of



Scheme 11 *Reagents and conditions:* i, $Ca(OCl)_2$, CH_3CN, 4 days, 80 °C

two stereoisomers of **25** in a 2:3 ratio and this is surprising, since the two tertiary CF_3 groups in **22** would be expected to exert a high degree of stereocontrol upon the geometry of epoxidation of the neighbouring double bond. Thus, the *cis*,*trans*-isomer **25a**, with $CF_3 \cdots CF_3$ interactions minimised, might be expected to be formed almost exclusively. Also surprising is the lack of any CF_3–CF_3 coupling in the spectrum, a phenomenon that has been observed in other similarly arranged systems.[17] The reason both diastereoisomers **25a** and **25b** are formed is thought to be due to the competing destabilising effect of eclipsing of the trifluoromethyl groups with the epoxide oxygen atom in **25a**.

Earlier workers in these laboratories have described the formation of a novel diepoxide **26** from the diene **1** in good yield (Scheme 12),[18] which on heating rearranged to give the per-



Scheme 12 *Reagents and conditions:* i, sealed tube, 200 °C, 24 h; ii, sealed tube, heat, 24 h

fluorinated dioxine **27**.[18] For comparison diepoxide **20** was dissolved in a small amount of diethyl ether, sealed in a quartz NMR tube and heated first at 100 °C and then in 50 °C increments up to 350 °C for 24 h at a time. At 300 °C the ^{19}F NMR spectrum revealed a small degree of decomposition of the starting diepoxide, and at 350 °C most of **20** had decomposed, with no formation of **28**. This comparison is puzzling, bearing in mind the ready rearrangement of **26** at 200 °C, and may be due to constraint placed on the system by the eight membered ring.

Experimental

^1H NMR Spectra were recorded on a Bruker AC250 spectrometer operating at 250.13 MHz or a Varian VXR400S spectrometer operating at 399.95 MHz. ^{19}F NMR Spectra were recorded on the Bruker AC250 spectrometer operating at 235.34 MHz or on the Varian VXR400S spectrometer operating at 376.29 MHz. ^{13}C NMR Spectra were recorded on a Bruker AC250 spectrometer operating at 62.9 MHz or a Varian VXR400S spectrometer operating at 100.58 MHz. All spectra were recorded with tetramethylsilane and fluorotrichloromethane as internal references. *J* Values are given in Hz. GLC Mass spectra were recorded on a VG 7070E spectrometer linked to a Hewlett Packard 5790A gas chromatograph fitted with a 25 m cross-linked methyl silicone capillary column. All mass-spectra were generated by electron impact (EI).

CAUTION: The unsaturated fluorocarbons described in this paper should be assumed to be toxic.

Reactions of diene 1 with aniline using caesium fluoride as a base

A mixture of diene **1** (3.00 g, 8.30 mmol), freshly distilled aniline (1.51 g, 16.11 mmol) and dry caesium fluoride (3.94 g, 25.71 mmol) in anhydrous acetonitrile (50 cm^3) was stirred at room temperature for 7 days. The mixture was then poured into water (150 cm^3) in a separating funnel. The organic products were extracted twice with diethyl ether (2 × 50 cm^3). The ethereal solutions were combined, dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Sublimation of the solid residue yielded 1-phenyl-2,3,4,5-tetrakis(trifluoromethyl)-pyrrole **2a**[19] (2.50 g, 6.02 mmol, 72%), mp 99–100 °C (lit.,[19] 98–99 °C) (Found: C, 40.4; H, 1.0; F, 54.7; N, 3.2. $C_{14}H_5F_{12}N$ requires C, 40.5; H, 1.2; F, 54.9; N, 3.4%); ν_{max}/cm^{-1} 1730m (C=C), 1200s–1280s (C–F), 3020 (Ar-H); δ_H(400 MHz; CD_3CN) 7.48 (m); δ_F(376 MHz; $CDCl_3$) −54.3 (6F, s, 2-CF_3 or 3-CF_3), −54.7 (6F, s, 2-CF_3 or 3-CF_3); *m/z* 415 (M^+, 100%) and 396 (28).

Reactions of diene 1 with aniline using potassium fluoride as a base

A mixture of diene **1** (3.00 g, 8.30 mmol), freshly distilled aniline (1.50 g, 16.11 mmol) and dry potassium fluoride (2.02 g, 34.56 mmol) in anhydrous acetonitrile (50 cm^3) was stirred at room temperature for 14 days. The mixture was then poured into water (150 cm^3) in a separating funnel. The organic products were extracted twice with diethyl ether (2 × 50 cm^3). The ethereal solutions were combined, dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Sublimation of the solid residue yielded 1-phenyl-2,3,4,5-tetrakis(trifluoromethyl)-pyrrole **2a** (2.20 g, 5.30 mmol, 63%) which was identified by comparison with an authentic sample (see above). The remaining solid was purified by recrystallisation from diethyl ether to give 1-*phenyl*-2,3,4-*tris*(*trifluoromethyl*)-1H-*pyrrolo*[3,2-c]*quinoline* **3a**† (0.35 g, 0.78 mmol, 8%), mp 229–230 °C (Found: C, 53.7; H, 2.0; F, 39.7; N; 6.0. $C_{20}H_9F_9N_2$ requires C, 53.6; H, 2.0; F, 38.1; N, 6.2%); ν_{max}/cm^{-1} 1730m (C=C), 1200s–1290s (C–F), 3020 (Ar-H); δ_H(250 MHz; $CDCl_3$) 6.83 (1H, d, $J_{6,5}$ 8.7, 5-H), 7.47 (1H, d, $J_{8,7}$ 7.7, 8-H), 7.80 (1H, m, 6-H), 7.82 (5H, m, phenyl ring), 8.27 (1H, d, $J_{7,8}$ 8.1, 7-H); δ_F(235 MHz; $CDCl_3$) −51.6 (3F, qq, $J_{3',2}$ 17.9 and $J_{3',2'}$ 11.1, 3′-CF_3), −52.9 (3F, q, $J_{2',3'}$ 11.1, 2′-CF_3), −63.9 (3F, q, $J_{2,3'}$ 17.9, 2-CF_3); *m/z* 448 (M^+, 100%) and 429 (13).

† The NMR spectra of the quinoline derivatives are assigned giving the quinoline ring unprimed numbers and the pyrrole ring primed numbers. See structure **3** in Scheme 3 for the numbering system.

Reaction of diene 1 with substituted anilines

With 4-dimethylaminoaniline. A mixture of diene **1** (3.00 g, 8.30 mmol), 4-dimethylaminoaniline (2.22 g, 16.52 mmol) and dry potassium fluoride (2.00 g, 34.50 mmol) in anhydrous acetonitrile (50 cm^3) was stirred at room temperature for 2 days. The mixture was then poured into water (150 cm^3) in a separating funnel. The organic products were then extracted twice with diethyl ether (2 × 50 cm^3). The ethereal solutions were combined, dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Sublimation yielded 1-(4′-*dimethylaminophenyl*)-2,3,4,5-*tetrakis*(*trifluoromethyl*)*pyrrole* **2b** (1.70 g, 3.71 mmol, 45%), mp 101–103 °C (Found: C, 42.0; H, 2.3; F, 50.1; N, 5.9. $C_{16}H_{10}F_{12}N_2$ requires C, 41.9; H, 2.2; F, 49.8; N, 6.1%); ν_{max}/cm^{-1} 1580m (Ar), 1740m (C=C), 1200s–1280s (C–F), 3020 (Ar-H); δ_H(250 MHz; $CDCl_3$) 3.04 [6H, s, $N(CH_3)_2$], 6.69 (2H, AB, *J* 9.1), 7.12 (2H, AB, *J* 9.1); δ_F(235 MHz; $CDCl_3$) −54.6 (6F, s, 2-CF_3 or 3-CF_3), −54.8 (6F, s, 2-CF_3 or 3-CF_3); *m/z* 458 (M^+, 80%) and 439 (28).

With 4-methoxyaniline. A mixture of diene **1** (3.00 g, 8.30 mmol), freshly sublimed 4-methoxyaniline (2.00 g, 16.30 mmol) and dry potassium fluoride (2.00 g, 34.50 mmol) in anhydrous acetonitrile (50 cm^3) was stirred at room temperature for 7 days. The mixture was then poured into water (150 cm^3) and the organic products were then extracted with diethyl ether (50 cm^3) which was dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Sublimation of the solid residue onto a cold finger yielded 1-(4′-methoxyphenyl)-2,3,4,5-tetrakis(trifluoromethyl)pyrrole **2c** (2.61 g, 5.86 mmol, 71%), mp 59–61 °C (Found: C, 40.2; H, 1.6; F, 50.8; N, 2.7. $C_{15}H_7F_{12}NO$ requires C, 40.5; H, 1.6; F, 51.2; N, 3.1%); ν_{max}/cm^{-1} 1730m (C=C), 1200s–1280s (C–F), 2850m (O–CH_3), 3020 (Ar-H); δ_H(250 MHz; $CDCl_3$) 3.89 (3H, s, OCH_3), 7.00 (2H, AB, *J* 8.8), 7.25 (2H, AB, *J* 8.8); δ_F(235 MHz; $CDCl_3$) −53.5 (6F, s, 2-CF_3 or 3-CF_3), −53.7 (6F, s, 2-CF_3 or 3-CF_3); *m/z* 445 (M^+, 100%) and 426 (38). The remaining solid was purified by recrystallisation from acetone–water to give 1-(4′-*methoxyphenyl*)-2,3,4-*tris*(*trifluoromethyl*)-8-*methoxy*-1H-*pyrrolo*[3,2-c]*quinoline* **3c**† (0.50 g, 0.98 mmol, 12%), mp 200–201 °C (Found: C, 51.9; H, 2.5; F, 33.7; N, 5.3. $C_{22}H_{13}F_9N_2O_2$ requires C, 52.0; H, 2.6; F, 33.6; N, 5.5%); ν_{max}/cm^{-1} 1730m (C=C), 1200s–1280s (C–F), 2850m (O–CH_3), 3020 (Ar-H); δ_H(250 MHz; $CDCl_3$) 3.43 (3H, s, OCH_3), 3.95 (3H, s, OCH_3), 6.23 (1H, s, 5-H), 7.18 (2H, AB, *J* 7.4), 7.26 (1H, s, 8-H), 7.44 (2H, AB, *J* 7.4), 8.15 (1H, d, $J_{7,8}$ 8.8, 7-H); δ_F(235 MHz; $CDCl_3$) −52.9 (3F, qq, $J_{3',2}$ 17.7 and $J_{3',2'}$ 11.2, 3′-CF_3), −54.1 (3F, q, $J_{2',3'}$ 11.2, 2′-CF_3), −64.7 (3F, q, $J_{2.3'}$ 17.7, 2-CF_3); *m/z* 508 (M^+, 100%) and 489 (9).

With 2-methoxyaniline. A mixture of diene **1** (3.00 g, 8.30 mmol), 2-methoxyaniline (2.00 g, 16.30 mmol) and dry potassium fluoride (2.00 g, 34.50 mmol) in anhydrous acetonitrile (50 cm^3) was heated under reflux, overnight, with continuous stirring. This was poured into water (150 cm^3) and acidified with hydrochloric acid and the organic products were then extracted with diethyl ether (50 cm^3), dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Sublimation yielded 1-(2′-*methoxyphenyl*)-2,3,4,5-*tetrakis*(*trifluoromethyl*)*pyrrole* **2d** (0.63 g, 1.24 mmol, 14%), mp 94–96 °C (Found: C, 41.0; H, 1.6; F, 50.3; N, 3.1. $C_{15}H_7F_{12}NO$ requires C, 40.5; H, 1.6; F, 51.2; N, 3.1%); ν_{max}/cm^{-1} 1730m (C=C), 1200s–1280s (C–F), 2850m (O–CH_3), 3020 (Ar-H); δ_H(250 MHz; $CDCl_3$) 3.82 (3H, s, OCH_3), 7.04 (1H, d, $J_{6',5'}$ 8.2, 6′-H), 7.06 (1H, dd, $J_{4',3'}$ 7.8 and $J_{4,'5'}$ 7.8, 4′-H), 7.26 (1H, d, $J_{3',4'}$ 7.8, 3′-H), 7.53 (1H, ddd, $J_{5',4'}$ 7.9, $J_{5',6'}$ 7.9 and $J_{5',3'}$ 1.6, 5′-H); δ_F(235 MHz; $CDCl_3$) −54.8 (6F, s, 2-CF_3 or 3-CF_3), −56.3 (6F, s, 2-CF_3 or 3-CF_3); *m/z* 445 (M^+, 100%) and 426 (67). The remaining solid was purified by recrystallisation from acetone–water to give 1-(2′-*methoxyphenyl*)-2,3,4-*tris*(*trifluoromethyl*)-6-*methoxy*-1H-*pyrrolo*[3,2-c]-*quinoline* **3d**† (1.66 g, 3.17 mmol, 37%), mp 201–202 °C (Found: C, 51.7; H, 2.4; F, 33.2; N, 5.2. $C_{22}H_{13}F_9N_2O_2$ requires C, 52.0; H, 2.6; F, 33.6; N, 5.5%); ν_{max}/cm^{-1} 1730m (C=C), 1200s–1280s (C–F), 2840m (O–CH_3), 3020 (Ar-H); δ_H(250 MHz; $CDCl_3$) 3.67 (3H, s, OCH_3), 4.09 (3H, s, OCH_3), 6.49 (1H, d, $J_{5,6}$ 8.3, 5-H), 7.07 (1H, d, $J_{3',4'}$ 7.7, 3′-H), 7.19 (1H, dd, $J_{5',4'}$ 8.1 and $J_{5',6'}$ 8.1, 5′-H), 7.24 (1H, d, $J_{6,5}$ 3.6, 6-H), 7.28 (1H, d, $J_{6',5'}$ 9.4, 6′-H), 7.44 (1H, d, $J_{7,6}$ 6.7, 7-H), 7.70 (1H, dd, $J_{4',3'}$ 8.0 and $J_{4',5'}$ 8.0, 4′-H); δ_F(235 MHz; $CDCl_3$) −52.9 (3F, qq, $J_{3',2}$ 17.9 and $J_{3',2'}$ 11.3, 3′-CF_3), −55.7 (3F, q, $J_{2',3'}$ 11.4, 2′-CF_3), −64.6 (3F, q, $J_{2,3'}$ 17.9, 2-CF_3); *m/z* 508 (M^+, 100%) and 489 (16).

With 3-methoxyaniline. A mixture of diene **1** (3.00 g, 8.30 mmol), 3-methoxyaniline (2.00 g, 16.33 mmol) and dry potassium fluoride (2.00 g, 34.50 mmol) in anhydrous acetonitrile (50 cm^3) was heated under reflux overnight with continuous stirring. This mixture was poured into water (150 cm^3), acidified with hydrochloric acid, then extracted with diethyl ether (50 cm^3). The ethereal extract was dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Sublimation yielded 1-(3′-*methoxyphenyl*)-2,3,4,5-*tetrakis*(*trifluoromethyl*)*pyrrole* **2e** (1.06 g, 2.38 mmol, 27%), mp 65–66 °C (Found: C, 40.5; H, 1.5; F, 50.9; N, 2.9. $C_{15}H_7F_{12}NO$ requires C, 40.5; H, 1.6; F, 51.2; N, 3.1%); ν_{max}/cm^{-1} 1730m (C=C), 1200s–1280s (C–F), 2850m (O–CH_3), 3020 (Ar-H); δ_H(250 MHz; $CDCl_3$) 3.99 (3H, s, OCH_3), 7.12 (1H, s, 2′-H), 7.19 (1H, d, $J_{6',5'}$ 7.9, 6′-H), 7.37 (1H, dd, $J_{4',5'}$ 9.4 and $J_{4',6'}$ 1.5, 4′-H), 7.70 (1H, dd, $J_{5',4'}$ 8.4 and $J_{5',6'}$ 8.4, 5′-H); δ_F(235 MHz; $CDCl_3$) −54.9 (6F, s, 2-CF_3 or 3-CF_3) −55.2 (6F, s, 2-CF_3 or 3-CF_3); *m/z* 445 (M^+, 100%) and 426 (41). The remaining solid was purified by recrystallisation from acetone–water to give a mixture (16:9) of two compounds (1.00 g, 1.97 mmol, 24%) (Found: C, 51.7; H, 2.6; F, 34.1; N, 5.4. $C_{22}H_{13}F_9N_2O_2$ requires C, 52.0; H, 2.6; F, 33.6; N, 5.5%); *m/z* 508 (M^+, 100%) and 489 (13). The mixture was found to contain 1-(3′-*methoxyphenyl*)-2,3,4-*tris*(*trifluoromethyl*)-9-*methoxy*-1H-*pyrrolo*[3,2-c]*quinoline* **3ei**† (*ca.* 15%); δ_H(250 MHz; $CDCl_3$) 3.19 (3H, s, OCH_3), 3.80 (3H, s, OCH_3), 6.80 (1H, s, 8-H), 6.84 (1H, s, 2′-H), 6.98 (1H, s, 6-H), 7.02 (1H, d, $J_{6',5'}$ 8.3, 6′-H), 7.07 (1H, s, 4′-H), 7.39 (1H, dd, $J_{5',4'}$ 8.1 and $J_{5',6'}$ 8.1, 5′-H), 7.91 (1H, d, $J_{7,8}$ 8.5, 7-H); δ_F(235 MHz; $CDCl_3$) −52.0 (3F, qq, $J_{3',2}$ 17.7 and $J_{3',2'}$ 11.3, 3′-CF_3), −53.8 (3F, q, $J_{2',3'}$ 11.3, 2′-CF_3), −65.1 (3F, q, $J_{2,3'}$ 17.7, 2-CF_3) and 1-(3′-*methoxyphenyl*)-2,3,4-*tris*(*trifluoromethyl*)-7-*methoxy*-1H-*pyrrolo*[3,2-c]*quinoline* **3eii**† (*ca.* 9%); δ_H(250 MHz; $CDCl_3$) 3.86 (3H, s, OCH_3), 3.93 (3H, s, OCH_3), 6.72 (1H, d, $J_{5,6}$ 9.3, 5-H), 6.88 (2H, s, 8-H and 2′-H, overlapping), 7.03 (1H, m, 6-H), 7.09 (1H, s, 6′-H), 7.58 (1H, dd, $J_{5',4'}$ 8.2 and $J_{5',6'}$ 8.2, 5′-H), 7.67 (1H, d, $J_{4',5'}$ 14.3, 4′-H); δ_F(235 MHz; $CDCl_3$) −52.9 (3F, qq, $J_{3',2}$ 17.6 and $J_{3',2'}$ 11.2, 3′-CF_3), −53.9 (3F, q, $J_{2',3'}$ 11.2, 2′-CF_3), −65.0 (3F, q, $J_{2,3'}$ 17.7, 2-CF_3).

With 4-fluoroaniline. A mixture of diene **1** (3.00 g, 8.30 mmol), 4-fluoroaniline (1.85 g, 16.32 mmol) and dry potassium fluoride (2.00 g, 34.50 mmol) in anhydrous acetonitrile (50 cm^3) was heated under reflux for 4 h with continuous stirring. The mixture was then poured into water (150 cm^3) in a separating funnel and acidified with hydrochloric acid. The organic products were then extracted with diethyl ether (50 cm^3), dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Sublimation yielded 1-(4′-*fluorophenyl*)-2,3,4,5-*tetrakis*-(*trifluoromethyl*)*pyrrole* **2f** (0.51 g, 1.18 mmol, 14%), mp 174–178 °C (Found: C, 38.6; H, 0.9; F, 57.5; N, 3.2. $C_{14}H_4F_{13}N$ requires C, 38.8; H, 0.9; F, 57.0; N, 3.2%); ν_{max}/cm^{-1} 1720m (C=C), 1200s–1280s (C–F), 3020 (Ar-H); δ_H(250 MHz; $CDCl_3$) 7.43 (2H, ABX, J_{AB} 9.3 and $J_{3'\text{-H,F}}$ 8.2, 3′-H), 7.57 (2H, ABX, J_{AB} 9.3 and $J_{2'\text{-H,F}}$ 4.7, 2′-H); δ_F(235 MHz; $CDCl_3$) −54.3 (6F, s, 2-CF_3 or 3-CF_3), −54.8 (6F, s, 2-CF_3 or 3-CF_3), −108.4 (1F, tt, $J_{F,3'\text{-H}}$ 7.8 and $J_{F,2'\text{-H}}$ 4.6, C_6H_4F); *m/z* 433 (M^+, 82%) and 414 (76). The remaining solid was purified by recrystallisation from acetone–water to give 1-(4′-*fluorophenyl*)-2,3,4-*tris*-(*trifluoromethyl*)-8-*fluoro*-1H-*pyrrolo*[3,2-c]*quinoline* **3f**† (0.55 g, 1.14 mmol, 12%), mp 217–218 °C (Found: C, 49.7; H, 1.3; F, 42.5; N, 5.6. $C_{20}H_7F_{11}N_2$ requires C, 49.6; H, 1.5; F, 43.2; N, 5.8%); ν_{max}/cm^{-1} 1730m (C=C), 1200s–1280s (C–F), 3020 (Ar-H); δ_H(250 MHz; $CDCl_3$) 6.55 (1H, dd, $J_{5,6}$ 11.0 and $J_{5,7}$

2.9, 5-H), 7.64 (2H, ABX, J_{AB} 9.2 and $J_{2'\text{-H,F}}$ 4.8, 2′-H), 7.71 (1H, dd, $J_{7,F}$ 8.8 and $J_{7,8}$ 8.8, 7-H), 7.74 (2H, ABX, J_{AB} 9.2 and $J_{3'\text{-H,F}}$ 8.5, 3′-H), 8.58 (1H, dd, $J_{8,7}$ 9.5 and $J_{8,F}$ 5.9, 8-H); δ_F(235 MHz; $CDCl_3$) −53.0 (3F, qq, $J_{3',2}$ 17.6 and $J_{3',2'}$ 10.8, 3′-CF_3), −54.0 (3F, q, $J_{2',3'}$ 11.0, 2′-CF_3), −65.0 (3F, q, $J_{2,3'}$ 17.5, 2-CF_3), −106.7 (1F, m, 6-F), −107.0 (1F, t, $J_{F,2'\text{-H}}$ 4.9, Ar-F); *m/z* 484 (M^+, 100%) and 465 (12).

With 4-chloroaniline. A mixture of diene **1** (3.00 g, 8.30 mmol), freshly sublimed 4-chloroaniline (2.10 g, 16.50 mmol) and dry potassium fluoride (2.00 g, 34.50 mmol) in anhydrous acetonitrile (50 cm^3) was heated under reflux for 3 h with continual stirring. The mixture was then poured into water (150 cm^3) in a separating funnel and extracted with diethyl ether (2 × 50 cm^3). The ethereal solutions were combined, dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Chromatography on silica gel with light petroleum (bp 40–60 °C)–diethyl ether–methanol (90:9:1) as the eluent followed by recrystallisation from hexane–diethyl ether yielded 1-(4′-*chlorophenyl*)-2,3,4,5-*tetrakis*(*trifluoromethyl*)*pyrrole* **2g** (0.33 g, 0.73 mmol, 7%), mp 136–137 °C (Found: C, 36.9; H, 0.8; Cl, 7.2; F, 50.0; N, 2.9. $C_{14}H_4ClF_{12}N$ requires C, 37.4; H, 0.9; Cl, 7.9; F, 50.7; N, 3.1%); ν_{max}/cm^{-1} 1730m (C=C), 1200s–1280s (C–F), 3020 (Ar-H); δ_H(250 MHz; $CDCl_3$) 7.30 (2H, AB, *J* 8.6), 7.52 (2H, AB, *J* 8.6); δ_F(235 MHz; $CDCl_3$) −54.2 (6F, s, 2-CF_3 or 3-CF_3), −54.8 (6F, s, 2-CF_3 or 3-CF_3); *m/z* 449 (M^+, 100%) and 430 (31).

With 4-nitroaniline. A mixture of diene **1** (3.00 g, 8.30 mmol), freshly sublimed 4-nitroaniline (2.35 g, 16.74 mmol) and dry potassium fluoride (2.00 g, 34.50 mmol) in anhydrous acetonitrile (50 cm^3) was heated under reflux for 4 h with continual stirring. The mixture was then poured into water (150 cm^3) and the organic products were then extracted with diethyl ether (2 × 50 cm^3). The ethereal solutions were combined, dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Chromatography on silica gel with light petroleum (bp 40–60 °C)–diethyl ether–methanol (90:9:1) as eluent followed by recrystallisation from diethyl ether yielded 1-(4′-*nitrophenyl*)-2,3,4,5-*tetrakis*(*trifluoromethyl*)*pyrrole* **2h** (0.31 g, 0.67 mmol, 9%), mp 171–172 °C (Found: C, 35.9; H, 0.7; F, 48.8; N, 5.9. $C_{14}H_4F_{12}N_2O_2$ requires C, 36.5; H, 0.9; F, 49.5; N, 6.1%); ν_{max}/cm^{-1} 1730m (C=C), 1200s–1280s (C–F), 1350s and 1550–1570s (C–NO_2), 3020 (Ar-H); δ_H(250 MHz; $CDCl_3$) 7.60 (2H, AB, *J* 8.6), 8.44 (2H, AB, *J* 8.6); δ_F(235 MHz; $CDCl_3$) −53.9 (6F, s, 2-CF_3 or 3-CF_3), −54.9 (6F, s, 2-CF_3 or 3-CF_3); *m/z* 460 (M^+, 100%) and 441 (19).

Reaction of diene 1 with ammonia

A mixture of the diene **1** (10.00 g, 27.61 mmol) and dry potassium fluoride (9.83 g, 169.06 mmol) in anhydrous THF (50 cm^3) was stirred for 7 days at room temperature while ammonia (2.00 g, 117.65 mmol) was introduced to the flask *via* a flexible gas reservoir. The mixture was filtered and the filtrate washed with more THF (50 cm^3), after which the solutions were combined and concentrated. Chromatography on alumina with dichloromethane as the eluent yielded (Z,Z)-2,5-*diaminoperfluoro*-3,4-*dimethylhexa*-2,4-*diene* **10** (1.52 g, 4.21 mmol, 16%), mp 21–23 °C (Found: C, 26.7; H, 1.1; N, 8.0. $C_8H_4F_{12}N_2$ requires C, 27.0; H, 1.1; N, 7.9%); ν_{max}/cm^{-1} 1730m (C=C), 1200s–1280s (C–F), 2250–2280m (NH_2); δ_H(250 MHz; $CDCl_3$) 4.66 (4H, br s); δ_F(235 MHz; $CDCl_3$) −61.6 (6F, psuedo sept., *J* 2.3), −67.0 (6F, psuedo sept., *J* 2.3); δ_C(100 MHz; $CDCl_3$) 90.6 [q, *J* 34.1, $NH_2C(CF_3)$=CCF_3], 119.2 [q, $J_{C,F}$ 277.9, $NH_2C(CF_3)$=CCF_3], 122.9 [q, $J_{C,F}$ 273.5, $NH_2C(CF_3)$=CCF_3], 140.1 [q, $J_{C,F}$ 32.3, $NH_2C(CF_3)$=CCF_3]; *m/z* 356 (M^+, 50%) and 337 (3). The remaining solid was separated by Kugelrohr distillation to give 2,4,5-*tris*(*trifluoromethyl*)-3-*cyanopyrrole* **11** (1.64 g, 5.54 mmol, 20%), mp 169–171 °C (Found: C, 32.4; H, 0.4; F, 58.7; N, 8.0. $C_8HF_9N_2$ requires C, 32.5; H, 0.3; F, 57.7; N, 9.5%); ν_{max}/cm^{-1} 1730m (C=C), 1200s–1280s (C–F), 2250m (CN); δ_H(250 MHz; $CDCl_3$) 7.86 (1H, br s); δ_F(235 MHz; $CDCl_3$) −55.8 (3F, q, $J_{5,4}$ 7.3, 5-CF_3), −58.7 (3F, q, $J_{4,5}$ 7.3, 4-CF_3), −59.8 (3F, s, 2-CF_3); δ_C(100 MHz; $CDCl_3$) 110.5 (s, CN), 117.6 (q, $J_{C,F}$ 39.7), 117.7 (q, $J_{C,F}$ 39.4), 119.8 (q, $J_{C,F}$ 270.2), 121.7 (q, $J_{C,F}$ 269.2), 124.3 (q, $J_{C,F}$ 270.2), 129.8 (q, $J_{C,F}$ 41.4); *m/z* 296 (M^+, 83%) and 277 (54), and 2,5-*diamino*-3,4-*dicyano*-1,1,1,6,6,6-*hexafluorohexa*-2,4-*diene* **12** (0.71 g, 2.63 mmol, 10%), mp 207–209 °C (decomp.) (Found: C, 35.1; H, 1.4; F, 41.2; N, 20.4. $C_8H_4F_6N_4$ requires C, 35.6; H, 1.5; F, 42.2; N, 20.7%); ν_{max}/cm^{-1} 1730m (C=C), 1200s–1280s (C–F), 2250m (CN); δ_H(250 MHz; $CDCl_3$) 7.09 (4H, br s); δ_F(235 MHz; $CDCl_3$) −65.9 (6F, s); δ_C(100 MHz; $CDCl_3$) 116.4 (s, CN), 121.0 (q, $J_{C,F}$ 278.5, CF_3), 147.1 (q, $J_{C,F}$ 32.3), 147.4 (q, $J_{C,F}$ 32.3); *m/z* 270 (M^+, 60%).

Reaction of perfluoro-3,4-dimethylhexa-2,4-diene 1 with catechol

Dried caesium fluoride (2.00 g, 13.16 mmol) was added to a sample of freshly sublimed catechol (0.36 g, 3.31 mmol) in acetonitrile (30 cm^3) and stirred in a sealable round-bottomed flask for 5 min. Diene **1** (1.00 g, 2.76 mmol) was then added under dry nitrogen and the mixture stirred for 7 days at room temperature. After this time recovered caesium fluoride, and other insoluble material, was filtered off to leave a clear yellow solution, which upon addition of a small amount of water (4 cm^3) gave an involatile clear lower layer. The lower layer was isolated and, after removal of residual solvent *in vacuo*, was identified as 2,3,4,5-*tetrakis*(*trifluoromethyl*)-1,6-*benzodioxocine* **18** (1.07 g, 2.49 mmol, 90%), bp 97 °C (Found: C, 38.7; H, 0.9. $C_{14}H_4F_{12}O_2$ requires C, 38.9; H, 0.9%); $\lambda_{max}(CH_2Cl_2)$/nm 229 (ε/dm^3 mol^{-1} cm^{-1} 25 425), 273 (12 075); ν_{max}/cm^{-1} 1730m (C=C), 1200s–1280s (C–F); δ_H(400 MHz; CD_3CN) 7.15 (2H, s), 7.16 (2H, s); δ_F(376 MHz; $CDCl_3$) −56.4 [6F, q, $J_{2,3}$ 12.0, OC(CF_3)=CCF_3], −65.0 [6F, q, $J_{3,2}$ 12.0, OC(CF_3)=CCF_3]; δ_C(100 MHz; $CDCl_3$) 107.5 [dq, $J_{C,F}$ 76.2 and $J_{C,F}$ 27.0, OC(CF_3)=CCF_3], 117.0 [q, $J_{C,F}$ 276.9, OC(CF_3)=CCF_3], 119.0 [q, $J_{C,F}$ 273.5, OC(CF_3)=CCF_3], 121.2 (s), 126.1 (s), 141.6 (s), 144.4 [q, $J_{C,F}$ 41.4, OC(CF_3)=CCF_3]; *m/z* 432 (M^+, 34%) and 413 (15).

Photochemical electrocyclisation of benzodioxocine derivative 18

A quartz Carius tube (60 cm^3) was charged with **18** (3.00 g, 6.94 mmol) and acetonitrile (10 cm^3), sealed *in vacuo* and agitated on a rotating arm under UV irradiation (broad band) for 24 h. The tube was opened and the material refrigerated (−15 °C) for 48 h, after which time a gel-like solid had fallen from solution. The material was isolated, residual solvent removed *in vacuo*, and identified as 3,4,5,6-*tetrakis*(*trifluoromethyl*)-2,7-*dioxatricyclo*-[6.4.0.0^{3,6}]*dodeca*-1(8),4,9,11-*tetraene* **22** (2.82 g, 6.52 mmol, 94%), bp 109 °C (Found: C, 38.5; F, 0.9. $C_{14}H_4F_{12}O_2$ requires C, 38.9; H, 0.9%); $\lambda_{max}(CH_2Cl_2)$/nm 265 (ε/dm^3 mol^{-1} cm^{-1} 2627); ν_{max}/cm^{-1} 1730m (C=C), 1200s–1280s (C–F); δ_H(400 MHz; CD_3CN) 6.93 (2H, AA′BB′, *J* 3.6 and 3.0), 7.01 (2H, AA′BB′, *J* 3.6 and 3.0); δ_F(376 MHz; $CDCl_3$) −63.9 [6F, t, *J* 12.0, OC(CF_3)–CCF_3], −73.4 [6F, t, *J* 12.0, OC(CF_3)–CCF_3]; δ_C(100 MHz; $CDCl_3$) 115.6 [q, $J_{C,F}$ 272.3, OC(CF_3)–CCF_3], 116.1 [s, OC(CF_3)–CCF_3], 118.1 (s), 118.5 [q, $J_{C,F}$ 287.5, OC(CF_3)–CCF_3], 126.3 (s), 138.7 (s); *m/z* 432 (M^+, 25%) and 413 (9).

Attempted thermal electrocyclisation of benzodioxocine derivative 18

A sample of **18** (0.25 g, 0.58 mmol) in acetonitrile (1 cm^3) was added to a quartz NMR tube which was heated gradually up to 180 °C over a period of 7 days. Repeated ^{19}F NMR analysis showed that no formation of **22** had occurred, with apparent decomposition of **18** in the upper temperature range.

Epoxidation of benzodioxocine derivative 18

Benzodioxocine **18** (3.00 g, 6.94 mmol), calcium hypochlorite (2.20 g, 15.38 mmol) and acetonitrile (10 cm^3) were stirred in a round-bottomed flask for 4 days at 80 °C. After filtration of unreacted calcium hypochlorite and other insoluble material, solvent was removed under reduced pressure to leave a mix-

ture of 3,5,6,7-tetrakis(trifluoromethyl)-2,4,8-trioxatricyclo-[7.4.0.0^{3,5}]trideca-1(9),6,10,12-tetraene **21** (30% yield by GLC); δ_F(376 MHz; $CDCl_3$) −56.7 [3F, br s, OC(CF_3)=CCF_3], −65.1 [3F, s, OC(CF_3)=CCF_3], −65.7 [3F, br s, OC(CF_3)(O)CCF_3], −70.7 [3F, s, OC(CF_3)(O)CCF_3]; *m/z* 448 (M^+, 81%), and diepoxide **20** (68% yield by GLC).

The reaction was repeated under similar conditions, but stirred for 7 days to give diepoxide **20** almost exclusively. Filtration and solvent removal were as above and the residue (2.58 g) was dissolved in a small amount of diethyl ether (5 cm^3) and refrigerated (−15 °C) for 2 days. A white precipitate was isolated and residual solvent removed under reduced pressure to give 3,5,6,8-tetrakis(trifluoromethyl)-2,4,7,9-tetraoxatetracyclo[8.4.0.0^{3,5}.0^{6,8}]tetradeca-1(10),11,13-triene **20** (2.31 g, 4.99 mmol, 72%), bp 62 °C (Found: C, 36.2; F, 0.7. $C_{14}H_4F_{12}O_4$ requires C, 36.2; H, 0.9%); ν_{max}/cm^{-1} 1730m (C=C), 1200s–1280s (C–F); δ_H(400 MHz; CD_3CN) 7.51 (2H, s), 7.53 (2H, s); δ_F(376 MHz; $CDCl_3$) −65.3 [6F, qt, $J_{2,3}$ 11.3 and J 1.1, OC(CF_3)(O)CCF_3], −69.1 [6F, q, $J_{3,2}$ 11.3, OC(CF_3)(O)CCF_3]; δ_C(100 MHz; $CDCl_3$) 63.7 [q, $J_{C,F}$ 40.9, OC(CF_3)(O)*C*CF_3], 82.8 [q, $J_{C,F}$ 43.2, O*C*(CF_3)(O)CCF_3], 120.3 [q, $J_{C,F}$ 282.5, OC(CF_3)(O)C*C*F_3], 120.5 [q, $J_{C,F}$ 279.9, OC(*C*F_3)(O)CCF_3], 123.9 (s), 129.7 (s), 143.5 (s); *m/z* 464 (M^+, 1%).

Epoxidation of 22

3,4,5,6-Tetrakis(trifluoromethyl)-2,7-dioxatricyclo[6.4.0.0^{3,6}]-dodeca-1(8),4,9,11-tetraene **22** (3.00 g, 6.94 mmol), calcium hypochlorite (1.20 g, 8.39 mmol) and acetonitrile (10 cm^3) were stirred in a round-bottomed flask for 4 days at room temperature. After filtration of unreacted calcium hypochlorite and other insoluble material, solvent was removed under reduced pressure to leave 3,4,6,7-tetrakis(trifluoromethyl)-2,5,8-trioxatetracyclo[7.4.0.0^{3,7}.0^{4,6}]trideca-1(9),10,12-triene **25** (2.55 g, 5.69 mmol, 82%), mp 69 °C (Found: C, 37.1; H, 0.7. $C_{14}H_4O_3F_{12}$ requires C, 37.5; H, 0.9%); ν_{max}/cm^{-1} 1730m (C=C), 1200s–1280s (C–F); δ_F(376 MHz; $CDCl_3$) major isomer −65.9 [6F, br s, OC(CF_3)–CCF_3], −72.0 [6F, s, OC(CF_3)–CCF_3]; minor isomer −66.3 [6F, br s, OC(CF_3)–CCF_3], −71.1 [6F, s, OC(CF_3)–CCF_3]; *m/z* 448 (M^+, 9%).

Attempted thermal ring opening of diepoxide 20

Diepoxide **20** (0.25 g, 0.54 mmol) in a solvating amount of diethyl ether (1 cm^3) was sealed in a quartz NMR tube *in vacuo*, and heated to 100 °C in a furnace for 24 h. By ^{19}F NMR spectroscopy there was no evidence for ring opening. The reaction was repeated at 150, 200, 250, 300 and 350 °C. At 300 °C the starting material appeared to be decomposing, as the intensity of the ^{19}F NMR spectrum reduced, and after heating at 350 °C almost complete decomposition had occurred.

References

1 Part 41: R. D. Chambers, W. K. Gray, J. F. S. Vaughan, S. R. Korn, M. Medibeille, J. A. K. Howard and A. Batsanov, *J. Chem. Soc., Perkin Trans. 1*, 1997, 135.
2 R. D. Chambers, M. W. Briscoe, S. J. Mullins, J. F. S. Vaughan, T. Nakamura and F. D. Drakesmith, *J. Chem. Soc., Perkin Trans. 1*, 1994, 3115.
3 R. D. Chambers, J. F. S. Vaughan, S. J. Mullins, T. Nakamura and A. J. Roche, *J. Fluorine Chem.*, 1995, **72**, 231.
4 D. P. Graham, *J. Org. Chem.*, 1966, **31**, 955.
5 H. C. Fielding and A. J. Rudge, *Br. Pat.*, 1 082 127 (1967).
6 A. Streitwieser and F. Mares, *J. Am. Chem. Soc.*, 1968, **90**, 2444.
7 R. D. Chambers, J. S. Waterhouse and D. L. H. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1977, 585.
8 J. W. Smith, *The Chemistry of the Amino Group*, Wiley Interscience, London, 1968.
9 M. R. Bryce, R. D. Chambers and G. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1984, 509.
10 D. H. Williams and I. Fleming, *Spectroscopic Methods in Organic Chemistry*, McGraw-Hill, Maidenhead, 1989.
11 E. A. Jauregui, F. H. Ferretti and C. A. Ponce, *Rev. Latinoam. Quim.*, 1975, 13.
12 W. Schroth, K. Kranke and J. Reinhardt, *Angew. Chem.*, 1963, **75**, 303.
13 W. Schroth, K. Kranke and J. Reinhardt, *Z. Chem.*, 1963, **3**, 119.
14 W. Schroth and B. Werner, *Angew. Chem., Int. Ed. Eng.*, 1967, **6**, 697.
15 R. D. Chambers, M. W. Briscoe, S. J. Mullins, J. F. S. Vaughan and T. Nakamura, *J. Chem. Soc., Perkin Trans. 1*, 1994, 3119.
16 R. D. Chambers, J. F. S. Vaughan and S. J. Mullins, *Res. Chem. Intermed.*, 1996, **22**, 703.
17 J. F. S. Vaughan, Ph.D. Thesis, University of Durham, 1994.
18 R. D. Chambers, J. F. S. Vaughan and S. J. Mullins, *J. Chem. Soc., Chem. Commun.*, 1995, 629.
19 Y. Kobayashi, A. Ando, K. Kawada, A. Ohsawa and I. Kumadaki, *J. Org. Chem.*, 1980, **45**, 2962.

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