ELSEVIER

Journal of Fluorine Chemistry 73 (1995) 189–202

JOURNAL OF FLUORINE CHEMISTRY

Unsaturated nitrogen compounds containing fluorine. Part 19. Cycloaddition reactions of 2,5-dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene with cycloalkenes and cyclodienes ☆

Mohammad M. Abdul-Ghani, Anthony E. Tipping *

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

Received 1 August 1994; accepted 15 December 1994

Abstract

Thermal reaction (20–70 °C) of the dichloroazine $CF_3CCl{=}NN{=}CClCF_3$, **2**, with cyclopentene (in CH_2Cl_2 solvent), cycloheptene, indene, acenaphthylene, 2,3-dihydrofuran, 3,4-dihydro-2*H*-pyran, norbornadiene, cyclopentadiene and dicyclopentadiene afforded, as the major product in each case, the corresponding rearranged [3+2] cycloadduct **3** containing a $CF_3CCl_2N<$ grouping. The direction of cycloaddition to the unsymmetrical carbocycles indene and cyclopentadiene was consistent with the reactions being LUMO (azine)–HOMO (dipolarophile) controlled. On attempted chromatographic purification on silica gel, the rearranged adducts **3** were hydrolysed to the corresponding amides **4** ($>NCCl_2CF_3 \rightarrow >NCOCF_3$). The cyclopentene reaction, unexpectedly, also gave the cyclopentadiene [3+2] cycloadduct **3b**, while from the norbornadiene reaction a hydrolysed 2:1 adduct **9** (4%) was isolated by chromatography. Other products obtained by chromatographic separation from the 3,4-dihydro-2*H*-pyran reaction were the substituted azine $\overbrace{CH_2(CH_2)_2OCH{=}C}\text{–}C(CF_3){=}NN{=}CClCF_3$ (**5**) (29%), equimolar amounts of the ketone $\overbrace{CH_2(CH_2)_2OCH{=}C}\text{–}COCF_3$ (**6**) (18%) and the chlorohydrazone $\overbrace{O(CH_2)_4CH}\text{–}NHN{=}CClCF_3$ (**7**) (18%), possibly arising via the [3+2] cycloadduct **15** of **5** and the pyran, and the hydrazone $\overbrace{CH_2(CH_2)_2OCH{=}C}\text{–}C(CF_3){=}NNH_2$ (**8**) (4%), formed via **15** or by hydrolysis of the amide **4g**.

Treatment of amide **4d**, derived from indene with ethanolic methylamine, gave the expected amino compound **21a** (94%) and $CF_3CONHMe$ (**22**) (91%). In contrast, treatment of the *exo*-amide **4h**, derived from norbornadiene with ethanolic methylamine, afforded the *N*-formyl compound **23** (87%), while corresponding treatment of a mixture of the *exo*- and *endo*-amides (**4h** and **4i**) gave the *exo*- and *endo*-amino compounds (**21b** and **21c**) (88%), together with compound **22** (ca. 10%) and the azapropenylindazole **24** (ca. 5%); compound **24** hydrolysed to **23** on storage. It is proposed that the amines **21b** and **21c** arose mainly via the sequence: $>NCOCF_3 \rightarrow >N\text{–}CH{=}NMe$ (**24**) $\rightarrow >NCHO$ (**23**) $\rightarrow >NH$.

Keywords: Unsaturated nitrogen compounds; Cycloaddition reactions; Dichlorohexafluorodiazahexadiene; NMR spectroscopy; IR spectroscopy; Mass spectrometry

1. Introduction

1,3-Dipolar [3+2] cycloadditions of hexafluoroacetone azine (**1**) with alkenes, alkynes and dienes have been investigated in detail, e.g. Refs. [3,4]. In a previous preliminary investigation to determine whether the dichloroazine **2** would undergo analogous [3+2] cycloaddition, it was observed that reaction did not take place with the open-chain dipolarophiles $CH_2{=}CHEt$, $CH_2{=}CMe_2$, $(NC)_2C{=}C(CN)_2$ or $HC{\equiv}CH$, but with cyclopentene a thick, black, multicomponent oil was formed, separation of which into its individual components was unsuccessful [5].

In the present work, the reaction of dichloroazine **2** with cyclopentene was reinvestigated in CH_2Cl_2 as solvent and the results obtained prompted a detailed investigation of the reactions of **2** with a range of cycloalkenes and cyclodienes.

$(CF_3)_2C{=}NN{=}C(CF_3)_2$ (**1**) $CF_3CCl{=}NN{=}CClCF_3$ (**2**)

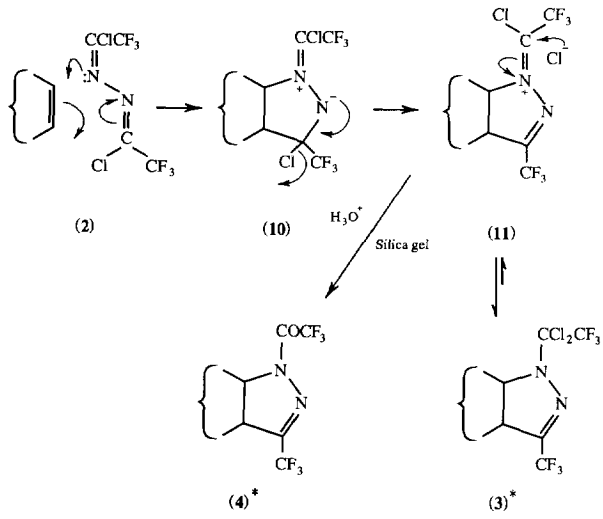
2. Results and discussion

The results obtained from reaction of the dichloroazine **2** with cycloalkenes and cyclodienes are summarised in Table 1.

☆ For part 18, see Ref. [1]; for preliminary communication, see Ref. [2].

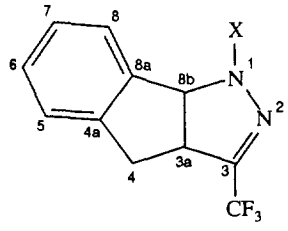
* Corresponding author.

SSDI 0022-1139(95)03227-4

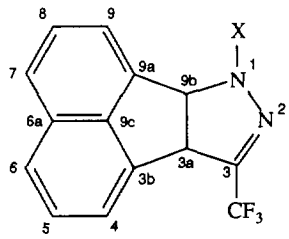


* Identified products.

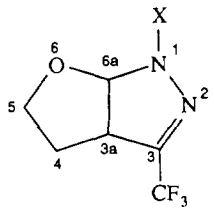
Scheme 1.



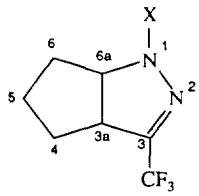
(3d) X = CCl_2CF_3
(4d) X = $COCF_3$



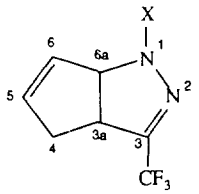
(3e) X = CCl_2CF_3
(4e) X = $COCF_3$



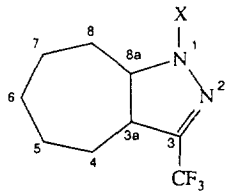
(3f) X = CCl_2CF_3
(4f) X = $COCF_3$



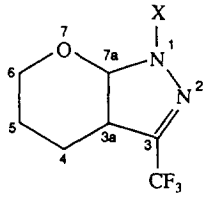
(3a) X = CCl_2CF_3
(4a) X = $COCF_3$



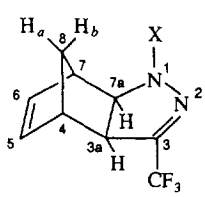
(3b) X = CCl_2CF_3
(4b) X = $COCF_3$



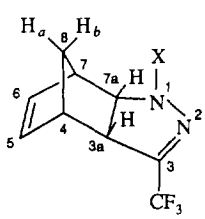
(3c) X = CCl_2CF_3
(4c) X = $COCF_3$



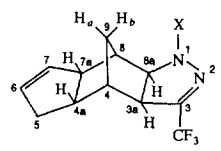
(3g) X = CCl_2CF_3
(4g) X = $COCF_3$



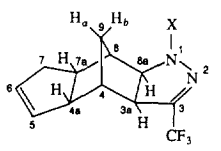
(3h) X = CCl_2CF_3
(4h) X = $COCF_3$



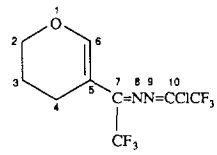
(3i) X = CCl_2CF_3
(4i) X = $COCF_3$



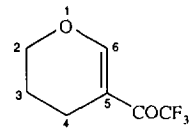
(3j) X = CCl_2CF_3
(4j) X = $COCF_3$



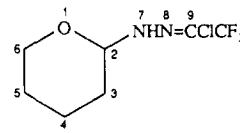
(3k) X = CCl_2CF_3
(4k) X = $COCF_3$



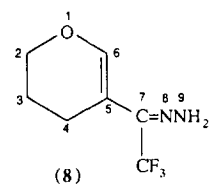
(5)



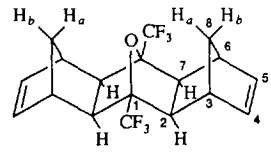
(6)



(7)



(8)



(9)

The rearranged 1:1 adducts **3** are considered to have been formed by initial [3+2] cycloaddition to afford the azomethine imides [10], followed by elimination of chloride ion and addition of chloride ion to the resulting immonium ions **11** (Scheme 1).

When solutions of the 1:1 adducts **3** in the eluting solvent were introduced on to the top of a column packed with silica gel prior to separation/purification by dry column flash chromatography (DCFC), evolution of hydrogen chloride was observed. This indicated that hydrolysis was taking place on the silica and so elution was not carried out for a period of 10–15 min to allow complete hydrolysis to occur. After elution, the products obtained from hydrolysis of the 1:1 adducts **3** were the amides **4** (Scheme 1), and this ready conversion can be explained by the adducts **3** being in equilibrium with the corresponding immonium ions **11** which would undergo facile hydrolysis.

The mixture of *exo* and *endo*-1:1 adducts **3h** and **3i** obtained from the reaction with norbornadiene was sufficiently pure to enable a satisfactory elemental analysis (for, C, H, N) to be obtained. The remaining compounds **3** were identified by a consideration of the IR, NMR and mass spectral data recorded for the crude non-volatile residues, although an accurate mass measurement was carried out on the cycloheptene adduct **3c**.

The cycloadducts **3** did not contain a strong absorption in their IR spectra at (ν_{max}) ca. 1500 cm^{-1} as expected for azomethine imides **10** and observed for azomethine imides derived from hexafluoroacetone azine (**1**) [3,4]. Furthermore, the ^{13}C NMR spectra contained an absorption in the range 98.9–88.9 (^2J=34.4–41.8 Hz) ppm as expected for N–CCl_2CF_3 and an absence of absorption for the immonium carbon in the $\overset{+}{\rangle}N{=}CClCF_3$ grouping of compounds **10** and **11** (expected δ_C: 140–160 ppm). Other relevant NMR absorptions were observed for the groups $\rangle$CH–N (δ_C: 73.4–65.7; 97.3, 86.8 ppm for O–CH–N in compounds **3f** and **3g**,

Table 1
Reaction of dichloroazine **2** with unsaturated carbocycles

Carbocycle	Molar ratio **2**/carbocycle	Conditions		Azine **2** recovered (%)	1:1 Adducts formed	Separated products [b] (%) [c]
		Temp. (°C)	Time (d)			
Cyclopentene [a]	1:1:1	70	21	23	**3a**; **3b**	**4a**(31); **4b**(4)
Cycloheptene	1:2	70	36	82	**3c**	**4c**(60)
Indene	1:1	70	4	22	**3d**	**4d**(93)
Acenaphthylene	2:1	70	12	88	**3e**	**4e**(67)
2,3-Dihydrofuran	1:2	50	3 h	23	**3f**	**4f**(93)
3,4-Dihydro-2*H*-pyran	1:1	70	3	35	**3g**	**4g**(32); **5**(29); **6**(18); **7**(18); **8**(4)
Norbornadiene	1:2	70	14	67	**3h**; **3i**	**4h**(80); **4i**(12); **9**(4)
Cyclopentadiene	1:1	20	8	43	**3b**; **3j**/**3k**	**4b**(71); **4j**/**4k** [d](5)
Dicyclopentadiene	1:1	40	16	32	**3j**/**3k**	**4j**/**4k** [d](76)

[a] In CH_2Cl_2 as solvent.
[b] After chromatography on silica.
[c] Based on dichloroazine **2** reacted.
[d] Present in 1:1 ratio, but not separated.

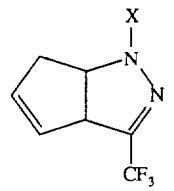
respectively), >CH–C(CF_3)=N [δ_C: 55.9–47.1 (>*C*H–); 152.1–146.5 (*C*=N, ^2J=32.8–38.9 Hz); 120.8–117.1 (CF_3, ^1J=267.3–274.5 Hz) ppm. δ_F: +11.6 to +16.7 ppm] and CCl_2CF_3 [δ_C: 125.7–115.7 (CF_3, ^1J=277.9–286.4 Hz) ppm. δ_F: +7.3 to −0.3 ppm], and all the compounds showed a molecular ion peak in their mass spectra. This data established that the 1:1 adducts had structure **3**.

The hydrolysis products, i.e. the amides **4**, gave satisfactory elemental analysis figures (for C, H, N, F) or accurate mass measurements and their structures were established by the following spectral data [IR (ν_{max}) (cm^{-1}): 1710–1730 (s) (C=O str.); 1620–1640 (m) (C=N str.); 1350–1365 (s) (=C–N str.); 1280–1100 (s) (C–F str.); 760–740 (m) (CF_3 def.). ^{1}H NMR δ_H: 5.03–4.42 (>CH–N) in compounds **4a**, **4c** and **4h–k**; 6.43–6.04 (O–CH–N) in compounds **4f** and **4g**; 6.60–5.62 (benzylic or allylic >CH–N) in compounds **4b**, **4d** and **4e**; 4.29–3.35 (>CH–C) in compounds **4a–d** and **4f–k**; 5.46 (benzylic >CH–C) ppm in compound **4e**. ^{13}C NMR δ_C: 71.3–62.3 (>CH–N); 92.3–85.4 (O–CH–N); 54.2–43.0 (>CH–C); 156.1–154.8 (CF_3C=O, ^2J=39.0–39.9 Hz); 116.3–115.4 (CF_3C=O, ^1J=283.0–287.4 Hz); 152.3–148.9 (CF_3C=N, ^2J=36.9–42.0 Hz); 120.3–117.8 (CF_3C=N, ^1J=271.7–272.9 Hz) ppm. ^{19}F NMR δ_F: +16.7 to +10.0 (CF_3C=N); +6.4 to +2.4 (CF_3C=O) ppm. MS: molecular ions present in all the spectra].

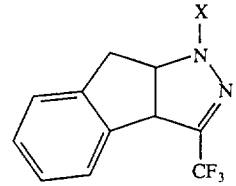
The *exo* stereochemistry of the amides **4h**, **4j** and **4k** was established via their H, H COSY NMR spectra, which showed four-bond coupling between the bridgehead protons H-3a/7a (**4h**) or H-3a/8a (**4j** and **4k**) and H-8a (**4h**) or H-9a (**4j** and **4k**) in the bridging CH_2 group, with the coupling involving a W pathway; no such coupling was observed for the *endo*-amide **4i**.

It has been reported that azidoximes undergo *exo* [3+2] cycloaddition to the norbornene double bond of dicyclopentadiene [6], but, in contrast, Diels–Alder [4+2] cycloaddition in chlorinated solvents involved reaction of the cyclopentene double bond [7]. In the present work, the NMR spectra clearly established that dichloroazine **2** had undergone [3+2] cycloaddition to the norbornene double bond, e.g. norbornene and cyclopentene vinylic protons would be expected to absorb in the ranges δ_H: 6.5–6.1 and 5.8–5.1 ppm, respectively [8]. The observed chemical shifts for the vinylic protons in compounds **4j** and **4k** were in the range 5.79–5.62 ppm.

The direction of addition of dichloroazine **2** to the unsymmetrical carbocycles cyclopentadiene and indene was established by the ^{1}H NMR spectra of the amides **4b** and **4d**, which showed coupling between H-3a and the adjacent CH_2 group (H-4) and ruled out the alternative structures **12** and **13**. The observed products are consistent with the reactions being LUMO (azine)–HOMO (dipolarophile) controlled. With dicyclopentadiene bidirectional addition took place and the two *exo* regioisomers **3j** and **3k**, isolated as the amides **4j** and **4k**, were formed in a 1:1 ratio, because the double bond in the cyclopentene ring was too remote to influence the cycloaddition.



(**12**) **a**; X = CCl_2CF_3
b; X = $COCF_3$



(**13**) **a**; X = CCl_2CF_3
b; X = $COCF_3$

The cyclopentadiene adduct **3b**, isolated as the amide **4b**, was an unexpected product from the cyclopentene reaction. The reactant cyclopentene did not contain cyclopentadiene (^{1}H NMR spectroscopy) and it is considered probable that compound **3b** arose via oxidation of cyclopentene to cyclopentadiene followed by reaction with dichloroazine **2**, but the

identity of the oxidizing agent is not known. Cyclopentadiene or its dimer were not detected in the recovered cyclopentene, but this is not surprising since they are more reactive towards dichloroazine **2** than is cyclopentene; cyclopentene did not react with **2** over 3 weeks at 20 °C.

Apart from amide **4g**, four other products **5–8** were isolated from the 3,4-dihydro-2*H*-pyran reaction, and possible routes by which they were formed are shown in Scheme 2.

The substituted azine **5** can arise from the initial [3+2] cycloadduct, azomethine imide **10g**, by dehydrochlorination of either the rearranged immonium chloride **11g** and/or the ring-opened hydrazone **14**. It has been reported that the azomethine imide formed by [3+2] cycloaddition of hexafluoroacetone azine (**1**) to 3,4-dihydro-2*H*-pyran underwent a spontaneous prototropic rearrangement to give the hydrazone $(CF_3)_2C{=}NNHC(CF_3)_2\overline{C{=}CHO(CH_2)_2}CH_2$, analogous to **14** [9].

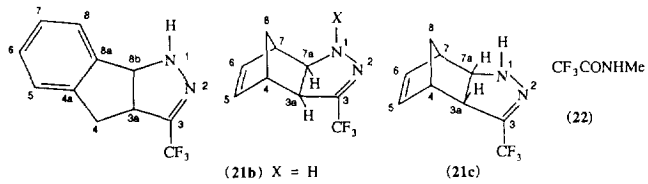
The remaining products **6–8** can then be formed via the [3+2] cycloadduct **15** of azine **5** and the pyran. Rearrangement and prototropic ring-opening of **15** would afford the immonium ions **16** and **17**, respectively, which on hydrolysis on silica gel would lead to the compounds **6**+**8** and **6**+**7**, respectively; the latter pathway is consistent with compounds **6** and **7** being formed in a 1:1 ratio. However, amide **4g** was observed to undergo slow hydrolysis, and elution from a DCFC column after contact with silica gel for 4 h gave hydrazone **8** (83%); this is an alternative pathway for the formation of **8** on DCFC separation of the mixture obtained from the dichloroazine **2**/3,4-dihydro-2*H*-pyran reaction.

Compounds **5–8** were identified on the basis of satisfactory elemental analysis figures, the presence of a molecular ion peak in the mass spectrum of each compound and the following spectral evidence. A 5-substituted-3,4-dihydro-2*H*-pyran ring was present in compounds **5**, **6** and **8** [δ_H: 7.76–6.89 (s, 1H, =CH–O, H-6); 4.15–3.64 (t, 2H, OCH_2, H-2); 2.65–2.15 (t, 2H, CH_2, H-4); 1.94–1.82 (tt, 2H, CH_2, H-3) ppm. δ_C: 162.3–154.3 (q, C-6, ^4J=2.3–5.4 Hz); 118.8–103.6 (C-5); 67.8–60.6 (C-2); 22.5–20.5 (C-4); 20.9–17.9 (C-3) ppm. IR (ν_{max}) (cm^{-1}): ca. 1610 (m) (C=C str.); 895–880 (m) (=CH out-of-plane bending)] together with the 5-substituents $-C(CF_3){=}NN{=}CClCF_3$ (**5**) [δ_F: +13.2 (3F, $CF_3C{=}N$); +7.7 (3F, $CF_3CCl{=}N$) ppm. δ_C: 148.1 (q, $CF_3C{=}N$, ^2J=32 Hz); 129.6 (q, $CF_3CCl{=}N$, ^2J=42 Hz); 120.0 (q, $CF_3C{=}N$, ^1J=278 Hz); 117.4 (q, $CF_3CCl{=}N$, ^1J=271 Hz) ppm. IR (ν_{max}) (cm^{-1}): 1640 (m) (C=N str.); 1250–1130 (s) (C–F str.); 970 (m) (C–Cl str.); 740 (m) (CF_3 def.)], $-COCF_3$ (**6**) [δ_F: +7.8 (CF_3) ppm. δ_C: 179.1 (q, $CF_3C{=}O$, ^2J=35 Hz); 116.7 (q, CF_3, ^1J=291 Hz) ppm. IR (ν_{max}) (cm^{-1}): 1680 (s) (C=O str.); 1240–1140 (s) (C–F str.); 750 (m) (CF_3 def.)] and $-C(CF_3){=}NNH_2$ (**8**) [δ_H: 3.96 (2H, NH_2) ppm. δ_F: 16.7 (CF_3) ppm. δ_C: 139.0 (q, $CF_3C{=}N$, ^2J=39 Hz); 121.7 (q, CF_3, ^1J=268 Hz) ppm. IR (ν_{max}) (cm^{-1}): 3280 (s) (N–H str.); 1490 (s) (C=N str.); 1210–1150 (s) (C–F str.); 710 (m) (CF_3 def.)]. Compound **7** was a 2-substituted tetrahydropyran [δ_H: 4.64 (mult., 1H, O–CH–N, H-2); 3.97/3.54 (AB, 2H, OCH_AH_B, H-6); 1.89 (mult., 2H, CH_2, H-3); 1.55 (mult., 4H, $2CH_2$, H-4/5) ppm. δ_C: 86.7 (C-2); 67.2 (C-6); 29.6 (C-3); 25.0/22.8 (C-4/5) with the 2-substituent being $-NHN{=}CClCF_3$ [δ_H: 6.4 (d, NH) ppm. δ_F: +9.4 ($CF_3CCl{=}N$) ppm. δ_C: 118.3 (q, CF_3, ^1J=272 Hz); 112.7 (q, $CF_3CCl{=}N$, ^2J=43 Hz) ppm. IR (ν_{max}) (cm^{-1}): 3240 (m) (N–H str.); 1610 (m) (C=N str.); 1210–1110 (s) (C–F str.); 1080 (s) (C–N str.); 890 (m) (C–Cl str.); 740 (m) (CF_3 def.)].

A minor product was isolated from the norbornadiene reaction by DCFC and was identified as having structure **9** by an accurate mass measurement and the following spectral data. It was symmetrical and consisted of two norbornene residues [δ_H: 6.14 (br., 4H, 2 CH=CH, H-4/5); 3.05 (br., 4H, 4 >CH, H-2/7); 2.02 (br., 4H, 4 CH, H-3/6); 2.18 (d, 2H, H-9a, J_{9a-9b}=9.0 Hz); 1.20 (dt, 2H, H-9b, J_{9a-9b}=9.0 Hz, $J_{2/7-9b}$=1.2 Hz) ppm. δ_C: 140.6 (C-4/5); 55.2 (C-3/6); 44.5 (q, C-2/7, ^3J=3.2 Hz); 42.7 (C-9) ppm] and two CF_3C groups linked by an oxygen bridge [δ_F: +8.5 (2 CF_3) ppm. δ_C: 125.4 (q, 2 CF_3, ^1J=281 Hz); 86.3 (q, 2 CF_3C–O, ^2J=32 Hz) ppm]. The H, H COSY spectrum confirmed that the compound had the *exo*, *exo* configuration by the presence of coupling involving a W pathway between H-2/7 and H-9b. The mass spectrum showed peaks at (*m*/*z*): 362 (100%, M^+); 296 [23, $(M-C_5H_6)^+$]; 230 [3, $(M-2C_5H_6)^+$]; 66 (71, $C_5H_6^+$) with the retro-Diels–Alder peaks at 296, 230 and 66 being entirely consistent with the proposed structure.

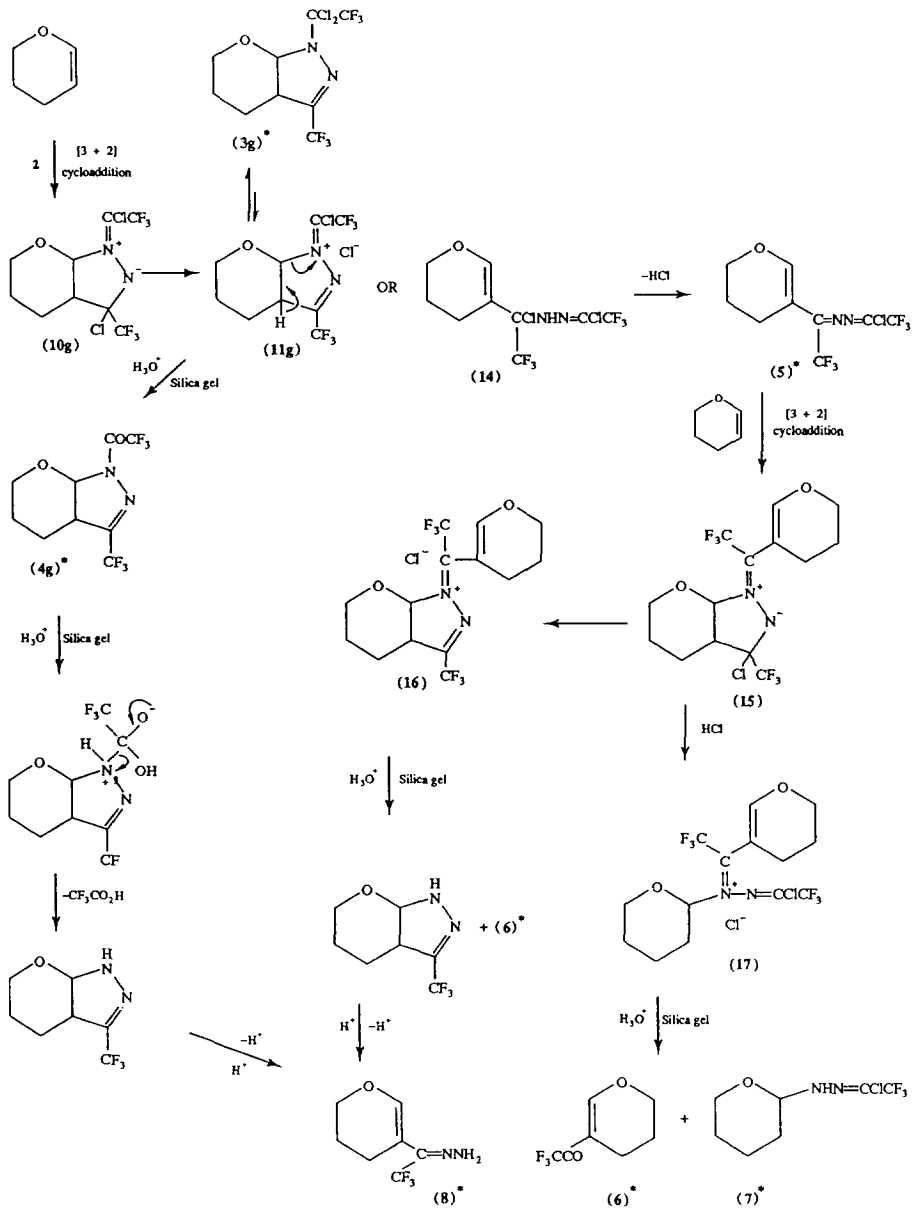
It is proposed that compound **9** arose from the initial [3+2] cycloadduct **10h** via the substituted azine **18** formed by analogous pathways to those postulated for the formation of azine **5** (Scheme 2). Cyclisation of azine **18** followed by dehydrochlorination afforded the intermediate pyridazine **19** which underwent Diels–Alder cycloaddition with norbornadiene. Elimination of nitrogen from the resulting adduct **20** followed by hydrolysis on silica gel gave the product **9** (Scheme 3).

It has been reported [10] that >NCOCF$_3$ groups are converted into >NH groups on reaction with primary amines. In the present work, the amides **4d**, **4h** and a mixture of **4h** and **4i** (ca. 1:1 molar ratio) were each treated with a large excess of an ethanolic solution of methylamine at room temperature in diethyl ether (0.5 h), and the results obtained are summarised in Table 2.



(21a) (21b) X = H (23) X = CHO (24) X = CH=NMe (21c) $CF_3CONHMe$ (22)

The indenoamide **4d** underwent reaction with methylamine as expected to give the amino compound **21a** and *N*-methyltrifluoroacetamide (**22**) in high yield (Scheme 4).



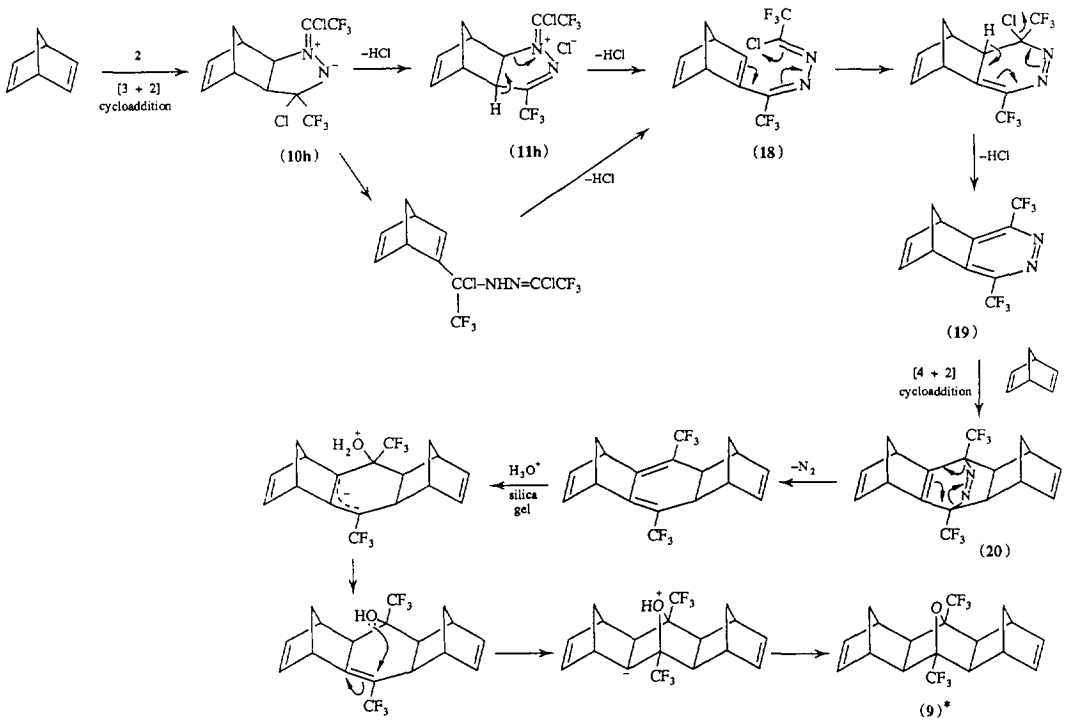
* Identified products.

Scheme 2.

However, the corresponding reaction of the *exo*-amide **4h** derived from norbornadiene afforded a high yield of the *N*-formyl compound **23** as the only product isolated. When the reaction was repeated using a mixture of the *exo*- and *endo*-amides **4h** and **4i** (ca. 1:1 molar ratio) and fresh ethanolic methylamine, the major products were the *exo*- and *endo*-amines **21b** and **21c**. A mixture of compound **22** (ca. 10%) and the azapropenylindazole **24** (ca. 5%) was also obtained and the indazole **24** was observed to hydrolyse to the *N*-formyl compound **23** on storage. Although the yield of the amines **21b** + **21c** was high, the isolated yield of the trifluoroacetamide **22** was very low, and so it is probable that the amines **21b** and **21c** arose mainly by a different route to that shown in Scheme 4.

It is proposed that amines **21b** and **21c** were formed via the intermediacy of compounds **23** and **24**, which requires the formal transfer of a hydride ion to the carbon atom of what was the carbonyl group in the reactant amides **4h** and **4i**. A more likely alternative to direct hydride transfer is a single-electron-transfer (SET) reaction followed by radical abstraction of a hydrogen atom (Scheme 5).

The proposed key intermediate is the imine **25** which undergoes reaction with methylamine either (i) by addition followed by elimination of fluoroform to give the guanidine derivative **26** or (ii) by direct loss of fluoroform to afford the nitrilium-type salt **27**. Fluoroform, which is highly volatile, would have been lost from the reaction mixture and would not have been detected.



* Identified products.

Scheme 3.

Table 2
Reaction of amides **4** with methylamine

Amide	Molar ratio $MeNH_2$/amide **4**	Products [a] (%) [b]
4d	10:1	**21a** (94); **22** (91)
4h	24:1	**23** (87)
4h/4i	25:1	**21b/21c** (88); **22** (ca. 10); **24** (ca. 5)

[a] After chromatographic purification/separation.
[b] Yields based on amide **4**.

An SET reaction between **26** and methylamine or internal hydride transfer involving the salt **27** would each lead to the azapropenylindazole **24**, hydrolysis of which would afford the *N*-formyl compound **23**. The amines **21b** and **21c** then arose via attack by ethanol on **23**.

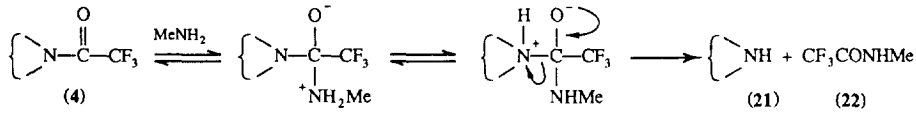
It is not apparent, however, why the reaction involving the *exo*-amide **4h** stopped at the *N*-formyl compound **23**, while the mixture of amides **4h** and **4i** gave amines **21b** and **21c**. Also, it is not clear why the amides **4h** and **4i** reacted differently from amide **4d**.

Compounds **21a**, **21b** + **21c**, **23** and **24** were identified by accurate mass measurements and the following spectral data. The NMR and IR spectra were analogous to those of the reactant amides **4d**, **4h** and **4i**, except for the absence of absorptions for the $>NCOCF_3$ group and the presence of absorptions for (i) $>NH$ [δ_H: ca. 5.4 (br., 1H) ppm. IR (ν_{max}) (cm^{-1}): 3340–3320 (m) (N–H str.)] in compounds **21**, (ii) $>N$–CHO [δ_H: 8.74 (s, 1H, O=C–H) ppm. δ_C: 160.9 (H–C=O) ppm. IR(ν_{max}) (cm^{-1}): 2880/2740 (m) (C–H str. in O=C–H); 1680 (s) (C=O str.)] in compound **23** and (iii) $>N$–CH=NMe [δ_H: 8.18 (s, 1H, N=CH); 3.20 (s, 3H, N–CH_3) ppm. δ_C: 139.3 (N=CH); 30.8 (N–CH_3) ppm] in compound **24**. *N*-Methyltrifluoroacetamide (**22**) gave the following spectral data which confirmed the structure [δ_H: 7.02 (br., 1H, NH); 2.91 (d, 3H, NCH_3, J_{NH-Me} = 4.8 Hz) ppm. δ_F: +1.8 ($COCF_3$) ppm. δ_C: 157.9 (q, CF_3C=O, ^2J = 37 Hz); 115.9 (q, CF_3 ^1J = 287 Hz) ppm. MS (*m/z*): 127 (85%, M^+); 69 (100, CF_3^+); 29 (5, CH_3N^+)].

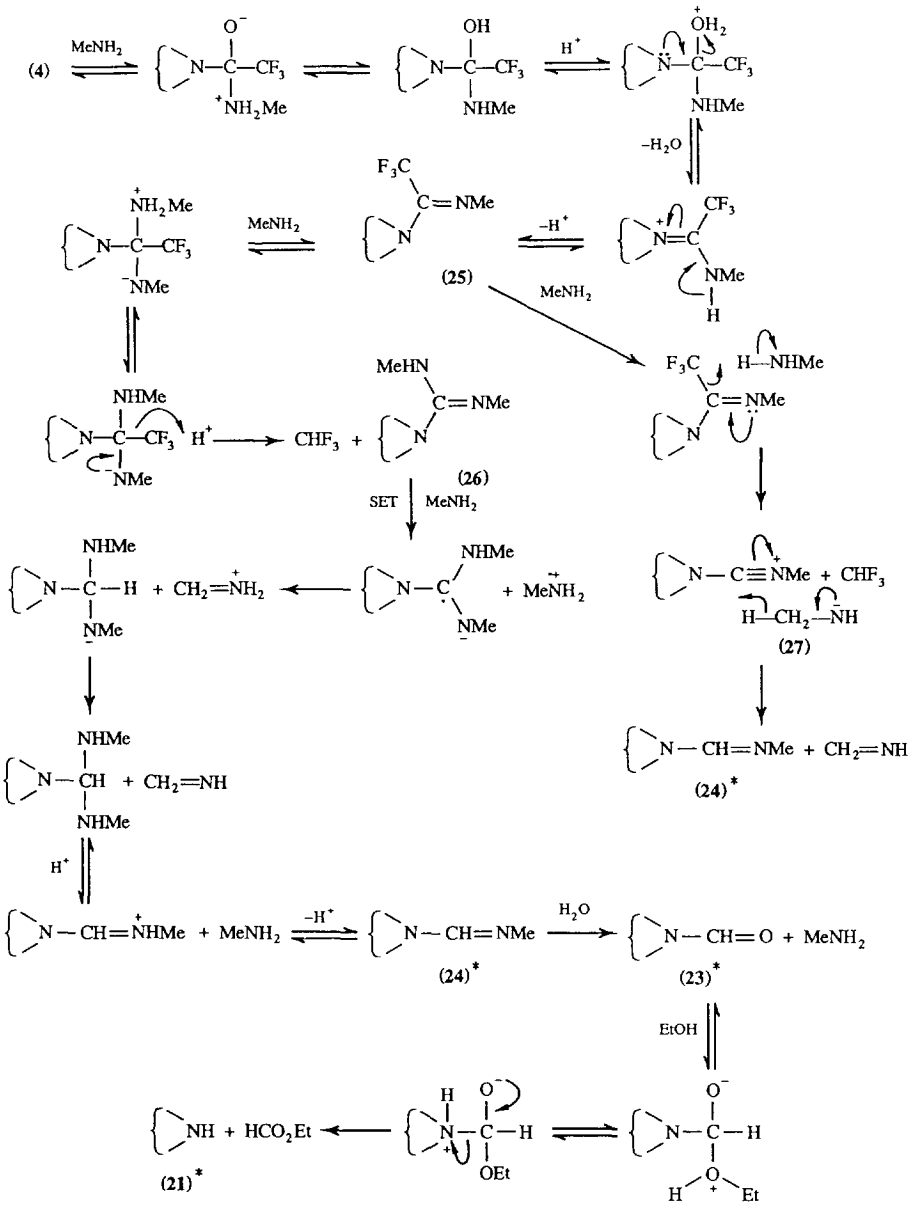
3. Experimental details

3.1. Starting materials

The dichloroazine **2** was synthesised by reaction of trifluoroacetic acid with hydrazine (2:1 molar ratio) to afford the



Scheme 4.



* Identified products.

Scheme 5.

bishydrazide $CF_3CONHNHCOCF_3$ which was treated with phosphoryl chloride and *N,N*-dimethylaniline hydrochloride [11,12]. Cyclopentadiene was prepared by thermal cracking of dicyclopentadiene at 200 °C and the other cycloalkenes and cyclodienes were commercial samples; the purity of each was confirmed (IR and ^{1}H NMR spectroscopy) before use.

3.2. General techniques

Reactions involving the dichloroazine **2** and the cycloalkenes/cyclodienes were carried out in Pyrex ampoules (50–100 cm^3) fitted with Rotaflo Teflon taps. The volatile material present after reaction was completed was transferred to a conventional vacuum system and was separated, where necessary, by fractional condensation at low pressure (ca. 2 mmHg) through traps cooled to progressively lower temperature. In cases where unchanged dichloroazine **2** and unchanged cycloalkene (or cyclodiene) condensed in the same trap, the composition of the mixture was determined by analytical gas–liquid chromatography (GLC) using a column (2 m) packed with Celite impregnated with Silicone SE30 oil (15% w/w) after calibration with a component mixture of known composition.

The non-volatile residues were examined by IR spectroscopy (Perkin-Elmer DE 783 instrument); ^{1}H NMR spectroscopy [Bruker AC-300 (300 MHz) spectrometer; external

reference Me_4Si]; ^{19}F NMR spectroscopy [Bruker AC-200 (188.3 MHz) instrument; external reference CF_3CO_2H]; ^{13}C NMR spectroscopy (including DEPT 135°) [Bruker AC-300 (75.0 MHz) instrument with broad-band proton-decoupling and D_2O as the deuterium lock signal; external reference Me_4Si]; and mass spectrometry [Kratos MS25 or MS45 instruments for low-resolution electron impact (EI), chemical ionisation (CI, NH_3 gas) or fast atom bombardment (FAB) spectra and a Kratos Concept IS instrument for accurate mass measurement, with all instruments operating at 70 eV]. The NMR spectra were recorded as solutions in $CDCl_3$ and chemical shifts to low field of reference are designated positive.

The non-volatile residues were then introduced on to the top of a column [packed with silica gel (Kieselgel 60 GF_{254})] used for dry column flash chromatography (DCFC) and after 10–15 min (to allow the 1:1 adducts **3** to hydrolyse completely) were then eluted (eluants as given in the text; light petroleum refers to the petroleum ether fraction, b.p. 30–40 °C). Further purification or separation of components was then achieved, where necessary, by repeated DCFC or by preparative-scale thin layer chromatography (TLC) [plates 23×20 cm coated with silica gel (Kieselgel 60 GF_{254}); eluants as given in the text]. The pure compounds were examined by IR, ^1H NMR (including H, H COSY), ^{19}F NMR and ^{13}C NMR spectroscopy and mass spectrometry (instruments as described previously).

Melting points are uncorrected.

3.3. Cycloaddition reactions of 2,5-dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (2)

(*a*) *With indene (general procedure)*

A mixture of the dichloroazine **2** (4.00 g, 15.32 mmol) and indene (1.78 g, 15.34 mmol) was introduced into a dry ampoule under a nitrogen atmosphere, the tube and contents were cooled to −196 °C and the tube was then evacuated and sealed. After warming to room temperature, the tube was heated at 70 °C (4 d) and the resulting volatile material on fractional condensation at low pressure (ca. 2 mmHg) in a conventional vacuum system gave a −45 °C fraction identified as unchanged dichloroazine **2** (0.89 g, 3.41 mmol, 22% recovered). Nitrogen was then introduced into the reaction tube and the residue (4.81 g) was shown (^{19}F NMR spectroscopy) to contain a single reaction product. The residue was identified (IR, NMR and mass spectroscopy) as a mixture of unchanged indene and 1-(1,1-dichloro-2,2,2-trifluoroethyl)-3-trifluoromethyl-3a,8b-dihydro-1*H*,4*H*-indeno-[1,2-*c*]pyrazole (**3d**) (nc) (Analysis: Found: M^+ 376/378/380. $C_{13}H_8Cl_2F_6N_2$ requires: M, 377). This residue was introduced on to the top of a DCFC column (70×55 mm) packed with silica gel (ca. 100 g) and hydrogen chloride was immediately evolved from the surface of the column. After 10 min, the material was eluted through the column (eluant: light petroleum.CH_2Cl_2 2:1 v/v) to afford (i) unchanged indene (0.33 g, 2.84 mmol, 19% recovered) and (ii) 1-trifluoroacetyl-3-trifluoromethyl-3a,8b-dihydro-1*H*,4*H*-indeno[1,2-*c*]pyrazole (**4d**) (nc) (3.58 g, 11.12 mmol, 93%) (Analysis: Found: C, 48.7; H, 2.4; N, 8.6; F, 35.7%; M^+, 322. $C_{13}H_8F_6N_2O$ requires: C, 48.4; H, 2.5; N, 8.7; F, 35.4%; M, 322), m.p. 105–107 °C.

(*b*) *With cyclopentene*

A mixture of the dichloroazine **2** (2.00 g, 7.66 mmol), cyclopentene (0.71 g, 8.25 mmol) and dichloromethane (5.32 g, 4.00 cm^3), heated at 70 °C (21 d) with the reaction monitored (^{19}F NMR spectroscopy), gave (i) a −196 °C fraction (5.49 g) identified (NMR and IR spectroscopy) as a mixture of unchanged cyclopentene (0.17 g, 2.10 mmol, 26% recovered) and dichloromethane (5.32 g), (ii) a −45 °C fraction identified as unchanged dichloroazine **2** (0.66 g, 2.53 mmol, 33% recovered) and (iii) a brown residue (1.71 g) which was shown (^{19}F NMR spectroscopy) to contain two major products (ratio 1.3:1.0) and a number of minor products. The two major products were identified (IR, NMR and mass spectroscopy) as 1-(1,1-dichloro-2,2,2-trifluoromethyl)-3-trifluoromethyl-3a,5,6,6a-tetrahydro-1*H*,4*H*-cyclopenta[1,2-*c*]pyrazole (**3a**) (nc) (Analysis: Found: M^+, 328/330/332. $C_9H_8Cl_2F_6N_2$ requires M, 329) and 1-(1,1-dichloro-2,2,2-trifluoroethyl)-3-trifluoromethyl-3a,6a-dihydro-1*H*,4*H*-cyclopenta[1,2-*c*]pyrazole (**3b**); the NMR and mass spectra of the latter product were identical to those of the same compound prepared by reaction of dichloroazine **2** with cyclopentadiene (see later).

The residue on DCFC (eluant: n-C_5H_{12}/CH_2Cl_2 2:1 v/v) gave four fractions, one containing the major products and the other three containing minor and decomposition products as shown by ^{19}F NMR spectroscopy. The major products were separated by preparative-scale TLC (same eluant) to give 1-trifluoroacetyl-3-trifluoromethyl-3a,5,6,6a-tetrahydro-1*H*,4*H*-cyclopenta[1,2-*c*]pyrazole (**4a**) (nc) (0.43 g, 1.57 mmol, 31%) (Analysis: Found: M^+, 274.0537. $C_9H_8F_6N_2O$ requires M, 274.0541) and 1-trifluoroacetyl-3-trifluoromethyl-3a,6a-dihydro-1*H*,4*H*-cyclopenta[1,2-*c*]pyrazole (**4b**) (0.33 g, 1.21 mmol, 24%), which was identified by a comparison of its IR, NMR and mass spectra with those of an authentic sample prepared from the reaction of dichloroazine **2** with cyclopentadiene.

Attempted reactions in the absence of solvent at 70 °C (24 h) and at 40 °C (2 d) gave unchanged reactants ca. 40% and ca. 75%, respectively, together with black non-volatile residues for which only a number of broad unresolved absorptions were observed in their ^1H and ^{19}F NMR spectra.

(*c*) *With cycloheptene*

A mixture of the dichloroazine **2** (4.00 g, 15.32 mmol) and cycloheptene (2.94 g, 30.63 mmol), heated at 70 °C (36 d), gave (i) a −45 °C fraction (5.98 g) which was identified as a mixture of unchanged dichloroazine **2** (3.29 g, 12.26 mmol, 80% recovered) and unchanged cycloheptene (2.68 g, 27.08 mmol, 88% recovered) and (ii) a dark brown residue (0.90 g) which was shown (^{19}F and ^{13}C NMR spectroscopy) to be slightly impure 1-(1,1-dichloro-2,2,2-trifluoroethyl)-3-trifluoromethyl-3a,4,5,6,7,8,8a-heptahydro-1*H*-cyclo-

hepta[1,2-*c*]pyrazole (**3c**) (nc). The residue on passage through a DCFC column (eluant: light petroleum/CH_2Cl_2 2:1 v/v) followed by purification by preparative-scale TLC (same eluant) gave 1-trifluoroacetyl-3-trifluoromethyl-3a,4,5,6,7,8,8a-heptahydro-1*H*-cyclohepta[1,2-*c*]pyrazole (**4c**) (nc) (0.49 g, 1.62 mmol, 60%) (Analysis: Found: M^+, 302.0851. $C_{11}H_{12}F_6N_2O$ requires: M, 302.0854).

(*d*) *With acenaphthylene*

A mixture of the dichloroazine **2** (4.00 g, 15.33 mmol) and acenaphthylene (1.17 g, 7.69 mmol), heated at 70 °C (12 d), gave (i) a −45 °C fraction, identified as unchanged dichloroazine **2** (3.76 g, 14.41 mmol, 88% recovered), and (ii) a dark brown residue (1.41 g), which was shown (^1H, ^{13}C and ^{19}F NMR spectroscopy) to consist of unchanged acenaphthylene and 1-(1,1-dichloro-2,2,2-trifluoroethyl)-3-trifluoromethyl-3a,9b-dihydro-1*H*-acenaphtho[1,2-*c*]pyrazole (**3e**) (nc). The residue on passage through a DCFC column (eluant: light petroleum/CH_2Cl_2 3:1 v/v) gave unchanged acenaphthylene (1.03 g, 6.78 mmol, 88% recovered) and a single product (0.32 g), which was purified by preparative-scale TLC (eluant: light petroleum/CH_2Cl_2 2:1 v/v) to afford 1-trifluoroacetyl-3-trifluoromethyl-3a,9b-dihydro-1*H*-acenaphtho[1,2-*c*]pyrazole (**4e**) (nc) (0.22 g, 0.61 mmol, 67%) (Analysis: Found: M^+ 358.0536. $C_{16}H_8F_6N_2O$ requires: M, 358.0541).

(*e*) *With 2,3-dihydrofuran*

A mixture of the dichloroazine **2** (4.00 g, 15.33 mmol) and 2,3-dihydrofuran (2.10 g, 30.00 mmol), heated at 50 °C (3 h), gave (i) a −78 °C fraction identified as unchanged 2,3-dihydrofuran (1.26 g, 18.0 mmol, 60% recovered), (ii) a −45 °C fraction identified as unchanged dichloroazine **2** (0.92 g, 3.52 mmol, 23% recovered) and (iii) a black residue (3.90 g) which was shown by TLC and ^{19}F NMR spectroscopy to contain one major component, one minor component and tar (base-line spot on TLC). The major component was identified as 1-(1,1-dichloro-2,2,2-trifluoroethyl)-3-trifluoromethyl-3a,4,5,6a-tetrahydro-1*H*-furano[2,3-*c*]pyrazole (**3f**) (nc) (ca. 3.4 g) (Analysis: Found: M^+, 330/332/334. $C_8H_6Cl_2F_6N_2O$ requires: M, 331). The residue on passage through a DCFC column (eluant: n-C_5H_{12}/CH_2Cl_2 1:1 v/v) gave a major product identified as 1-trifluoroacetyl-3-trifluoromethyl-3a,4,5,6a-tetrahydro-1*H*-furano[2,3-*c*]pyrazole (**4f**) (nc) (3.04 g, 11.01 mmol, 93%) (Analysis: Found: C, 34.8; H, 2.2; N, 10.1; F, 41.2%; M^+, 276. $C_8H_6F_6N_2O_2$ requires: C, 34.8; H, 2.2; N, 10.1; F, 41.3%; M, 276) and a minor unidentified product (0.24 g) which was impure and could not be purified by preparative-scale TLC (same eluant).

(*f*) *With 3,4-dihydro-2H-pyran*

A mixture of the dichloroazine **2** (4.00 g, 15.33 mmol) and the pyran (1.30 g, 15.50 mmol), heated at 70 °C (3 d), gave a −45 °C fraction (1.88 g) identified as a mixture of unchanged dichloroazine **2** (1.42 g, 5.44 mmol, 35% recovered) and unchanged pyran (0.46 g, 5.47 mmol, 35% recovered) and a black residue (3.41 g) which was shown (^{13}C and ^{19}F NMR spectroscopy) to contain a number of products including 1-(1,1-dichloro-2,2,2-trifluoroethyl)-3-trifluoromethyl-3a,5,6,7a-tetrahydro-1*H*,4*H*-pyrano[2,3-*c*]pyrazole (**3g**) (nc). The residue on passage through a DCFC column (eluant: light petroleum/CH_2Cl_2 2:1 v/v) gave the following products: (i) 5-(2-chloro-1,1,1,6,6,6-hexafluoro-3,4-diaza-hexa-2,4-dien-5-yl)-3,4-dihydro-2*H*-pyran (**5**) (nc) (0.89 g, 2.88 mmol, 29%) (Analysis: Found: C, 35.1; H, 2.5; N, 9.3; F, 36.9%; M^+ 308/310. $C_9H_7ClF_6N_2O$ requires: C, 35.0; H, 2.3; N, 9.1; F, 36.9%; M, 308.5); (ii) 5-trifluoroacetyl-3,4-dihydro-2*H*-pyran (**6**) (nc) (0.32 g, 1.78 mmol, 18%) (Analysis: Found: C, 45.2; H, 4.0; F, 31.9%; M^+, 180. $C_7H_7F_3O_2$ requires: C, 45.6; H, 3.8; F, 31.7%; M, 180); (iii) a liquid (0.45 g) which was further purified by preparative-scale TLC (eluant: light petroleum/Et_2O 3:1 v/v) to afford 2-(1-chloro-2,2,2-trifluoroethylidenehydrazonyl)-2,3,5,6-tetrahydro-2*H*-pyran (**7**) (nc) (0.39 g, 1.70 mmol, 18%) (Analysis: Found: C, 37.1; H, 4.3; N, 12.5; F, 24.9%; M^+ 230/232. $C_7H_{10}ClF_3N_2O$ requires: C, 36.7; H, 3.9; N, 12.2; F, 24.8%; M, 230.5); (iv) 1-trifluoroacetyl-3-trifluoromethyl-3a,5,6,7a-tetrahydro-1*H*,4*H*-pyrano[2,3-*c*]pyrazole (**4g**) (nc) (0.93 g, 3.21 mmol, 32%) (Analysis: Found: M^+, 290.0502. $C_9H_8F_6N_2O$ requires: M, 290.0490); and (v) 5-[1-(2,2,2-trifluoroethylidenehydrazono)]3,4-dihydro-2*H*-pyran (**8**) (nc) (0.09 g, 0.46 mmol, 4%) (Analysis: Found: C, 43.1; H, 4.8; N, 14.6%; M^+, 194. $C_7H_9F_3N_2O$ requires: C, 43.3; H, 4.6; N, 14.4%; M, 194).

(*g*) *With norbornadiene*

A mixture of the dichloroazine **2** (4.20 g, 16.09 mmol) and norbornadiene (2.82 g, 30.65 mmol), heated at 70 °C (18 h), gave volatile material (5.12 g) which was identified as a mixture of unchanged dichloroazine **2** (2.80 g, 10.73 mmol, 67% recovered) and unchanged norbornadiene (2.32 g, 25.22 mmol, 82% recovered), and a non-volatile residue (1.86 g) which was shown (^1H, ^{13}C, ^{19}F NMR and mass spectroscopy) to be a mixture of the two isomers (ratio 67:10) *exo*-1-(1,1-dichloro-2,2,2-trifluoroethyl)-3-trifluoromethyl-3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indazole (**3h**) (nc) and the corresponding *endo* compound (**3i**) (nc) (1.86 g, 5.27 mmol) (Analysis: Found: C, 37.7; H, 2.3; N, 7.6%; M^+, 352/354/356. $C_{11}H_8Cl_2F_6N_2$ requires: C, 37.3; H, 2.3; N, 7.9%; M, 353). The mixture was passed through a DCFC column (eluant: n-C_6H_{14}/CH_2Cl_2 2:1 v/v) when the following products were obtained: (i) *exo*-1-trifluoroacetyl-3-trifluoromethyl-3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indazole (**4h**) (nc) (1.28 g, 4.29 mmol, 80%) (Analysis: Found: C, 44.0; H, 3.0; N, 9.7; F, 38.3%; M^+, 298. $C_{11}H_8F_6N_2O$ requires: C, 44.3; H, 2.7; N, 9.4; F, 38.2%; M, 298); (ii) *endo*-1-trifluoroacetyl-3-trifluoromethyl-3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indazole (**4i**) (nc) (0.19 g, 0.64 mmol, 12%) (Analysis: Found: C, 44.3; H, 3.0; N, 9.5; F, 38.2%; M^+, 298. $C_{11}H_8F_6N_2O$ requires: C, 44.3; H, 2.7; N, 9.4; F, 38.2%; M, 298); and (iii) *exo,exo*-1,8-bis(trifluoromethyl)-15-oxahexacyclo[6.6.1.1.^{3,6}1.^{10,13}0.^{2,7}0^{9,14}]heptadeca-4,11-diene (**9**) (nc) (0.08 g, 0.22 mmol, 4%) (Analysis: Found: M^+, 362.1095. $C_{18}H_{16}F_6O$ requires: M, 362.1105).

Table 3
^{1}H, ^{19}F and ^{13}C NMR spectral data

Compound	NMR δ (ppm) [a]
3a	δ_F: +12.1 (3F, CF_3-3); +1.8 (3F, CF_3CCl_2). δ_C: 151.2 (q, C-3, ^2J=38.9 Hz); 119.7 (q, CF_3-3, ^1J=274.6 Hz); 115.7 (q, CF_3CCl_2, ^1J=286.4 Hz); 93.4 (q, CCl_2, ^2J=39.8 Hz); 65.7 (C-6a); 49.1 (C-3a); 36.1 (C-6); 30.8 (C-4); 23.0 (C-5).
3b	δ_F: +12.0 (3F, CF_3-3); +1.9 (3F, CF_3CCl_2). δ_C: 148.8 (q, C-3, ^2J=36.2 Hz); 133.5 (C-6); 127.9 (C-5); 120.3 (q, CF_3CCl_2, ^1J=284.1 Hz); 120.0 (q, CF_3-3, ^1J=271.6 Hz); 88.9 (q, CCl_2, ^2J=32.6 Hz); 68.4 (C-6a); 47.1 (C-3a); 35.6 (C-4).
3c	δ_F: +12.9 (3F, CF_3-3); +3.4 (3F, CF_3CCl_2). δ_C: 148.5 (q, C-3, ^2J=38.9 Hz); 120.4 (q, CF_3CCl_2, ^1J=279.8 Hz); 118.3 (q, CF_3-3, ^1J=271.4 Hz); 98.8 (q, CCl_2, ^2J=36.6 Hz); 66.8 (C-8a); 48.9 (C-3a); 29.2 (C-8); 27.8/26.8/26.7/26.4 (C-4/5/6/7).
3d	δ_F: +13.2 (3F, CF_3-3); +7.3 (3F, CF_3CCl_2). δ_C: 151.7 (q, C-3, ^2J=36.9 Hz); 140.7 (C-8a); 138.0 (C-4a); 129.9 (C-8); 128.1/127.4/124.8 (C-5/6/7); 118.8 (q, CF_3CCl_2, ^1J=280.1 Hz); 118.6 (q, CF_3-3, ^1J=274.5 Hz); 98.3 (q, CCl_2, ^2J=38.2 Hz); 77.3 (C-8b); 49.5 (C-3a); 34.6 (C-4).
3e [b]	δ_F: +11.8 (3F, CF_3-3); +3.3 (3F, CF_3CCl_2). δ_C: 152.1 (q, C-3, ^2J=37.8 Hz); 119.9 (q, CF_3CCl_2, ^1J=281.5 Hz); 119.4 (q, CF_3-3, ^1J=272.7 Hz); 97.5 (q, CCl_2, ^2J=38.5 Hz); 73.4 (C-9b); 54.9 (C-3a).
3f	δ_F: +16.7 (3F, CF_3-3); −0.3 (3F, CF_3CCl_2). δ_C: 146.5 (q, C-3, ^2J=37.3 Hz); 120.1 (q, CF_3CCl_2, ^1J=284.6 Hz); 119.5 (q, CF_3-3, ^1J=271.7 Hz); 97.3 (C-6a); 94.6 (q, CCl_2, ^2J=37.6 Hz); 66.7 (C-5); 48.9 (C-3a); 29.7 (C-4).
3g [c]	δ_F: +15.6 (3F, CF_3-3); +1.7 (3F, CF_3CCl_2). δ_C: 147.6 (q, C-3, ^2J=32.8 Hz); 120.7 (q, CF_3-3, ^1J=274.4 Hz); 119.7 (q, CF_3CCl_2, ^1J=277.9 Hz); 94.7 (q, CCl_2, ^2J=38.0 Hz); 86.8 (C-7a).
3h	δ_H: 6.33 (dd, 1H, H-6, J_{5-6}=5.5 Hz, J_{7-6}=3.0 Hz); 6.17 (dd, 1H, H-5, J_{6-5}=5.5 Hz, J_{4-5}=3.0 Hz); 4.44 (d, 1H, H-7a, J_{3a-7a}=9.1 Hz); 3.52 (dd, 1H, H-3a, J_{7a-3a}=9.1 Hz, J_{9a-3a}=1.0 Hz); 3.34 (br., 1H, H-7); 3.27 (br., 1H, H-4); 1.78 (d pentet, 1H, H-8a, J_{8b-8a}=10.0 Hz, J=1.6 Hz); 1.57 (d mult., 1H, H-8b, J_{8a-8b}=10.0 Hz). δ_F: +11.1 (3F, CF_3-3); +2.7 (3F, CF_3CCl_2). δ_C: 148.5 (q, C-3, ^2J=36.8 Hz); 140.8 (C-6); 136.6 (C-5); 121.1 (q, CF_3CCl_2, ^1J=283.4 Hz); 120.8 (q, CF_3-3, ^1J=272.0 Hz); 98.3 (q, CCl_2, ^2J=37.7 Hz); 73.4 (C-7a); 55.9 (C-3a); 50.6 (C-7); 46.5 (C-4); 44.2 (C-8).
3i	δ_H: 6.23 (dd, 1H, H-6, J_{5-6}=5.8 Hz, J_{7-6}=3.2 Hz); 6.17 (dd, 1H, H-5, J_{6-5}=5.8 Hz, J_{4-5}=3.0 Hz); 4.89 (dd, 1H, H-7a, J_{3a-7a}=10.5 Hz, J_{7-7a}=4.0 Hz); 3.88 (mult., 1H, H-3a); 3.44 (mult., 1H, H-4); 1.64 (dt. 1H, H-8a, J_{8b-8a}=9.0 Hz, J_{3a-8a}=J_{7a-8a}=1.8 Hz); 1.45 (d mult., 1H, H-8b, J_{8a-8b}=9.0 Hz). δ_F: +10.6 (3F, CF_3-3); +2.4 (3F, CF_3CCl_2). δ_C: 148.2 (q, C-3, ^2J=37.2 Hz); 140.5 (C-6); 136.7 (C-5); 125.7 (q, CF_3CCl_2, ^1J=280.1 Hz); 120.7 (q, CF_3-3, ^1J=271.2 Hz); 98.0 (q, CCl_2, ^2J=37.6 Hz); 71.7 (C-7a); 55.4 (C-3a); 49.2 (C-7); 48.7 (C-4); 45.7 (C-8).
3j/3k	δ_F: 11.8/11.5 (2×3F, CF_3-3); 6.2/6.15 (2×3F, CF_3CCl_2). δ_C: 150.9/149.7 (2q, C-3, ^2J=38.5/36.4 Hz); 136.8/134.6 (C-7A/5B); 133.0/128.6 (C-6); 122.8/120.9 (2q, CF_3CCl_2, ^1J=284.1/283.4 Hz); 120.6/117.1 (2q, CF_3-3, ^1J=272.6/267.3 Hz); 96.8/89.4 (2q, CCl_2, ^2J=41.8/34.4 Hz); 72.0/67.2 (C-8a); 53.3/52.3 (C-3a); 51.4/51.3 (C-8); 46.7/45.8 (C-7a); 43.4/42.3/41.9/40.6 (C-4/4a); 36.8/36.6 (C-5A/7B); 33.0/32.2 (C-9).
4a	δ_H: 4.92 (dd mult., 1H, H-6a, J_{3a-6a}=10.0 Hz, J_{6A-6a}=9.2 Hz); 3.78 (dd mult., 1H, H-3a, J_{6a-3a}=10.0 Hz, J_{4A-3a}=9.2 Hz); 2.10 (mult., 2H, H-6); 1.84 (mult., 4H, H-4/5). δ_F: +12.1 (3F, CF_3-3); +6.3 (3F, CF_3CO). δ_C: 154.9 (q, C=O, ^2J=39.2 Hz); 151.7 (q, C-3, ^2J=37.1 Hz); 119.6 (q, CF_3-3, ^1J=272.5 Hz); 115.6 (q, CF_3CO, ^1J=283.0 Hz); 65.6 (C-6a); 49.1 (C-3a); 36.2 (C-6); 30.9 (C-4); 23.9 (C-5).
4b	δ_H: 6.04 (mult., 2H, H-5/6); 5.62 (d, 1H, H-6a, J_{3a-6a}=9.9 Hz); 4.07 (dd mult., 1H, H-3a, J_{6a-3a}=9.9 Hz, J_{4-3a}=9.1 Hz); 2.86 (mult., 2H, H-4). δ_F: +12.1 (3F, CF_3-3); +6.3 (CF_3CO). δ_C: 155.6 (q, C=O, ^2J=39.5 Hz); 151.4 (q, C-3, ^2J=36.9 Hz); 134.6 (C-6); 125.7 (C-5); 119.6 (q, CF_3-3, ^1J=272.5 Hz); 115.6 (q, CF_3CO, ^1J=286.9 Hz); 71.3 (C-6a); 45.8 (C-3a); 36.2 (C-4).
4c	δ_H: 4.68 (mult., 1H, H-8a); 3.64 (mult., 1H, H-3a); 2.10–1.35 (complex, 10H, H-4/5/6/7/8). δ_F: +12.1 (3F, CF_3-3); +6.3 (3F, CF_3CO). δ_C: 155.4 (q, C=O, ^2J=39.4 Hz); 149.1 (q, C-3, ^2J=37.8 Hz); 118.3 (q, CF_3-3, ^1J=273.8 Hz); 115.6 (q, CF_3CO, ^1J=287.4 Hz); 64.7 (C-8a); 48.8 (C-3a); 30.2 (C-8); 27.4/27.1/26.6/25.5 (C-4/5/6/7).
4d	δ_H: 7.78 (dd, 1H, H-8, J_{7-8}=9.0 Hz, J_{6-8}=2.0 Hz); 7.37 (td, 1H, H-7, J_{8-7}=J_{6-7}=9.0 Hz, J_{5-7}=2.0 Hz); 7.34 (td, 1H, H-6, J_{5-6}=J_{7-6}=9.0 Hz, J_{8-6}=2.0 Hz); 7.29 (dd, 1H, H-5, J_{6-5}=9.0 Hz, J_{7-5}=2.0 Hz); 6.25 (d, 1H, H-8b, J_{3a-8b}=10.0 Hz); 4.29 (dddd, 1H, H-3a, J_{4A-3a}=12.0 Hz, J_{8b-3a}=10.0 Hz, J_{4B-3a}=4.5 Hz, J=1.0 Hz); 3.47/3.41 (ABX, 2H, H-4A/4B, J_{4A-4B}=18.0 Hz, J_{3a-4A}=12.0 Hz, J_{3a-4B}=4.5 Hz). δ_F: +12.2 (3F, CF_3-3); +6.3 (3F, CF_3CO). δ_C: 156.1 (q, C=O, ^2J=39.5 Hz); 151.9 (q, C-3, ^2J=37.0 Hz); 140.8 (C-8a); 138.4 (C-4a); 130.7 (C-8); 128.9 (C-7); 128.0 (C-6); 125.6 (C-5); 120.3 (q, CF_3-3, ^1J=272.8 Hz); 116.3 (q, CF_3CO, ^1J=287.1 Hz); 70.5 (C-8b); 47.9 (C-3a); 35.2 (C-4).
4e	δ_H: 7.98 (d, 1H, H-9, J_{8-9}=7.5 Hz); 7.87 (d, 1H, H-4, J_{5-4}=8.5 Hz); 7.84 (dd, 1H, H-7, J_{8-7}=6.5 Hz, J_{6-7}=2.8 Hz); 7.59 (complex, 3H, H-5/6/8); 6.60 (d, 1H, H-9b, J_{3a-9b}=9.6 Hz); 5.46 (d, 1H, H-3a, J_{9b-3a}=9.6 Hz). δ_F: +13.4 (3F, CF_3-3); +6.3 (3F, CF_3CO). δ_C: 155.4 (q, C=O, ^2J=39.9 Hz); 148.9 (q, C-3, ^2J=37.8 Hz); 138.4 (C-9a); 136.9 (C-9c); 135.8 (C-3b); 131.8 (C-6a); 128.9/128.4 (C-4/7); 125.6/124.6 (C-6/8); 121.9 (C-5); 119.6 (q, CF_3-3, ^1J=272.7 Hz); 115.9 (q, CF_3CO, ^1J=287.3 Hz); 68.5 (C-9b); 54.8 (C-3a).
4f	δ_H: 6.43 (d, 1H, H-6a, J_{3a-6a}=7.2 Hz); 4.21 (ABdd, 1H, H-5a, J_{5B-5A}=9.5 Hz, J_{4A-5A}=7.0 Hz, J_{4B-5A}=1.0 Hz); 3.97 (dd, 1H, H-3a, J_{4B-3A}=7.5 Hz, J_{6a-3a}=7.2 Hz); 3.51 (dABd, 1H, H-5B, J_{4B-5B}=12.0 Hz, J_{5A-5B}=9.5 Hz, J_{4A-5B}=5.0 Hz); 2.37 (ABdd, 1H, H-4A, J_{4B-4A}=11.5 Hz, J_{5A-4A}=7.0 Hz, J_{5B-4A}=5.0 Hz); 2.16 (dABdd, 1H, H-4B, J_{5B-4B}=12.0 Hz, J_{4A-4B}=11.5 Hz, J_{3a-4B}=7.5 Hz, J_{5A-4B}=1.0 Hz). δ_F: +12.8 (3F, CF_3-3); +6.8 (3F, CF_3CO). δ_C: 155.3 (q, C=O, ^2J=39.8 Hz); 149.2 (q, C-3, ^2J=37.5 Hz); 119.2 (q, CF_3-3, ^1J=272.4 Hz); 115.4 (q, CF_3CO, ^1J=287.3 Hz); 92.3 (C-6a); 66.9 (C-5); 48.5 (C-3a); 29.2 (C-4).
4g	δ_H: 6.04 (d, 1H, H-7a, J_{3a-7a}=7.7 Hz); 3.68 (t, 2H, H-6, J_{5-6}=7.5 Hz); 3.40 (d mult., 1H, H-3a, J_{7a-3a}=7.7 Hz); 2.21/2.06 and 1.80/1.66 (2AB mult., 4×1H, H-4A/4B/5A/5B). δ_F: +13.2 (3F, CF_3-3); +7.7 (3F, CF_3CO). δ_C: 155.9 (q, C=O, ^2J=39.2 Hz); 151.7 (q, C-3, ^2J=37.6 Hz); 119.9 (q, CF_3-3, ^1J=272.7 Hz); 116.2 (q, CF_3CO, ^1J=287.3 Hz); 85.4 (C-7a); 61.4 (C-6); 43.0 (C-3a); 20.5 (C-5); 17.8 (C-4).
4h	δ_H: 6.29 (dd, 1H, H-6, J_{5-6}=5.6 Hz, J_{7-6}=3.0 Hz); 6.17 (dd, 1H, H-5, J_{6-5}=5.6 Hz, J_{4-5}=3.0 Hz); 4.61 (d, 1H, H-7a, J_{3a-7a}=8.5 Hz); 3.52 (br., 1H, H-7); 3.47 (d, 1H, H-3a, J_{7a-3a}=8.5 Hz); 3.28 (br., 1H, H-4); 1.67 (d mult., 1H, H-8a, J_{8b-8a}=10.0 Hz); 1.35 (d, 1H, H-8b, J_{8a-8b}=10.0 Hz). δ_F: +10.7 (3F, CF_3-3); +5.9 (3F, CF_3CO). δ_C: 156.1 (q, C=O, ^2J=39.1 Hz); 150.4 (q, C-3, ^2J=37.6 Hz); 139.6 (C-6); 136.8 (C-5); 120.2 (q, CF_3-3, ^1J=271.7 Hz); 116.3 (q, CF_3CO, ^1J=287.2 Hz); 68.7 (C-7a); 54.2 (C-3a); 47.4 (C-7); 46.5 (C-4); 43.8 (C-8).

(continued)

Table 3 (*continued*)

Compound	NMR δ (ppm) [a]
4i	δ_H: 6.14 (dd, 1H, H-6, J_{5-6}=5.5 Hz, J_{7-6}=3.0 Hz); 6.02 (dd, 1H, H-5, J_{6-5}=5.5 Hz, J_{4-5}=3.0 Hz); 5.03 (dd, 1H, H-7a, J_{3a-7a}=10.0 Hz, J_{7-7a}=4.0 Hz); 3.87 (ddd, 1H, H-3a, J_{7a-3a}=10.0 Hz, J_{4-3a}=4.2 Hz, J_{8a-3a}=1.0 Hz); 3.67 (br., 1H, H-7); 3.35 (br., 1H, H-4); 1.69 (d mult., 1H, H-8a, J_{8b-8a}=9.5 Hz); 1.47 (d, 1H, H-8b, J_{8a-8b}=9.5 Hz). δ_F: +10.0 (3F, CF_3-3); +5.8 (3F, CF_3CO). δ_C: 154.9 (q, C=O, ^2J=39.2 Hz); 150.2 (q, C-3, ^2J=37.8 Hz); 136.4 (C-6); 134.0 (C-5); 117.8 (q, CF_3-3, ^1J=279.9 Hz); 115.7 (q, CF_3CO, ^1J=287.2 Hz); 66.4 (C-7a); 52.4 (C-3a); 49.0 (C-7); 46.6 (C-4); 45.8 (C-8).
4j/4k	δ_H: 5.79 [dd mult., 1H, H-7 (**4j**), J_{6-7}=5.5 Hz, J_{7a-7}=2.5 Hz]; 5.72 [br., 2H, H-5/6 (**4k**)]; 5.62 [dd, mult., 1H, H-6 (**4j**), J_{7-6}=5.5 Hz, J_{5A-6}=2.5 Hz]; 4.42/4.36 (2× d mult., 2×1H, H-8a, J_{3a-8a}=9.0/8.5 Hz); 3.35 (mult., 1H)/3.27 (mult., 3H)/3.04 (mult., 1H)/2.74 (complex, 4H)/2.58 (mult., 1H)/2.40 (complex, 3H)/2.23 (mult., 1H)[H-3a/4/4a/5 (**4j**)/7 (**4k**)/7a/8]; 1.58 (d mult., 2H, H-9a, J_{9b-9a}=11.5 Hz); 1.35 (d mult., 2H, H-9b, J_{9a-9b}=11.5 Hz). δ_F: +11.87/11.51 (2×3F, CF_3-3); +6.2/+6.15 (2×3F, CF_3CO). δ_C: 154.8/154.6 (2q, C=O, ^2J=38.5/39.0 Hz); 152.3/151.8 (2q, C-3, ^2J=41.8/42.0 Hz); 132.7/131.6 [C-7 (**4j**)/C-5 (**4k**)]; 130.9/130.7 (C-6); 119.6 (q, CF_3-3, ^1J=272.6 Hz); 115.6 (q, CF_3CO, ^1J=287.4 Hz); 65.1/62.3 (C-8a); 51.6/50.7 (C-3a); 49.9/46.7 (C-8); 45.0/44.7 (C-7a); 42.9/42.8 (C-4); 40.9/40.0 (C-4a); 35.0/34.7 [C-5 (**4j**)/C-7 (**4k**)]; 32.3/32.1 (C-9).
5	δ_H: 6.89 (1H, H-6); 4.04 (t, 2H, H-2, J_{3-2}=5.2 Hz); 2.15 (t, 2H, H-4, J_{3-4}=6.0 Hz); 1.84 (tt, 2H, H-3, J_{4-3}=6.0 Hz, J_{2-3}=5.2 Hz). δ_F: +13.2 (3F, CF_3-7); +7.7 (3F, CF_3-10). δ_C: 154.3 (q, C-6, ^4J=2.3 Hz); 148.1 (q, C-7, ^2J=32.3 Hz); 129.6 (q, C-10, ^2J=42.1 Hz); 120.0 (q, CF_3-7, ^1J=277.9 Hz); 117.4 (q, CF_3-10, ^1J=271.2 Hz); 103.6 (C-5); 66.7 (C-2); 21.3 (C-4); 20.9 (C-3).
6	δ_H: 7.76 (1H, H-6); 4.15 (t, 2H, H-2, J_{3-2}=5.5 Hz); 2.33 (t, 2H, H-4, J_{3-4}=6.5 Hz); 1.94 (tt, 2H, H-3, J_{4-3}=6.5 Hz, J_{2-3}=5.5 Hz). δ_F: +7.8 (CF_3CO). δ_C: 179.1 (q, C=O, ^2J=34.6 Hz); 162.3 (q, C-6, ^4J=5.4 Hz); 116.7 (q, CF_3, ^1J=291.1 Hz); 111.2 (C-5); 67.8 (C-2); 20.5 (C-4); 17.9 (C-3).
7	δ_H: 6.48 (d, 1H, NH, H-7, J_{2-7}=7.0 Hz); 4.64 (mult., 1H, H-2); 3.97/3.54 (AB mult., 2H, H-6A/6B, J_{6A-6B}=14.6 Hz); 1.89 (mult., 2H, H-3); 1.55 (complex, 4H, H-4/5). δ_F: +9.4 (CF_3-10). δ_C: 118.3 (q, CF_3-10, ^1J=271.5 Hz); 112.7 (q, C-10, ^2J=42.9 Hz); 86.7 (C-2); 67.2 (C-6); 29.6 (C-3); 25.0/22.8 (C-4/5).
8	δ_H: 7.43 (1H, H-6); 3.96 (br., 2H, NH_2); 3.64 (t, 2H, H-2, J_{3-2}=7.0 Hz); 2.65 (t, 2H, H-4, J_{3-4}=7.5 Hz); 1.82 (tt, 2H, H-3, J_{4-3}=7.5 Hz, J_{2-3}=7.0 Hz). δ_F: +16.7 (CF_3-7). δ_C: 158.7 (q, C-6, ^4J=3.6 Hz); 139.0 (q, C-7, ^2J=36.1 Hz); 121.7 (q, CF_3-7, ^1J=268.4 Hz); 118.5 (C-5); 60.6 (C-2); 22.5 (C-4); 18.5 (C-3).
9	δ_H: 6.14 (br., 2H, H-4/5); 3.05 (br., 2H, H-2/7); 2.02 (br., 2H, H-3/6); 2.18 (d, 1H, H-8a, J_{8b-8a}=9.0 Hz); 1.20 (dt, 1H, H-8b, J_{8a-8b}=9.0 Hz, J_{2-8b}=J_{3-8b}=1.2 Hz). δ_F: +8.5 (CF_3). δ_C: 140.6 (C-4/5); 125.4 (q, CF_3, ^1J=280.5 Hz); 86.3 (q, C-1, ^2J=31.6 Hz); 55.2 (C-3/6); 44.5 (q, C-2/7, ^3J=3.2 Hz); 42.7 (C-8).
21a	δ_H: 7.21 (4H, H-4/5/6/7); 5.45 (br., 1H, NH); 5.33 (d, 1H, H-8b, J_{3a-8b}=9.2 Hz); 3.98 (mult., 1H, H-3a); 3.26 (d, 2H, H-4, J_{3a-4}=5.8 Hz). δ_F: +13.4 (CF_3-3). δ_C: 142.7 (q, C-3, ^2J=34.9 Hz); 141.0/140.9 (C-4a/8a); 128.9/127.7/124.9/123.7 (C-5/6/7/8); 121.2 (q, CF_3-3, ^1J=270.4 Hz); 69.8 (C-8b); 47.5 (C-3a); 35.5 (C-4).
21b	δ_H: 6.22 (dd, 1H, H-6, J_{5-6}=6.0 Hz, J_{7-6}=3.0 Hz); 6.03 (dd, 1H, H-5, J_{6-5}=6.0 Hz, J_{4-5}=3.0 Hz); 5.40 (br., 1H, NH); 4.22 (d, 1H, H-7a, J_{3a-7a}=9.8 Hz); 3.39 (d, 1H, H-3a, J_{7a-3a}=9.8 Hz); 3.21 (br., 1H, H-7); 3.01 (br., 1H, H-4); 1.49 (d mult., 1H, H-8a, J_{8b-8a}=8.8 Hz); 1.26 (d mult., 1H, H-8b, J_{8a-8b}=8.8 Hz). δ_F: +12.1 (CF_3-3). δ_C: 140.8 (q, C-3, ^2J=38.3 Hz); 136.4 (C-6); 134.2 (C-5); 121.3 (q, CF_3-3, ^1J=269.6 Hz); 68.9 or 66.5 (C-7a); 54.0 or 53.4 (C-3a); 50.7 or 47.2 (C-7); 47.7 or 43.1 (C-8); 46.2 or 45.9 (C-4).
21c	δ_H: 6.06 (2H, H-5/6); 5.40 (br., 1H, NH); 4.57 (d, 1H, H-7a, J_{3a-7a}=9.0 Hz); 3.78 (d, 1H, H-3a, J_{7a-3a}=9.0 Hz); 3.24 (br., 1H, H-7); 3.19 (br., 1H, H-4); 1.60 (mult., 2H, H-8a/8b). δ_F: +11.5 (CF_3-3). δ_C: 140.8 (q, C-3, ^2J=38.3 Hz); 136.0 (C-5/6); 121.6 (q, CF_3-3, ^1J=271.4 Hz), 68.9 or 66.5 (C-7a); 54.0 or 53.4 (C-3a); 50.7 or 47.2 (C-7); 47.7 or 43.1 (C-8); 46.2 or 45.9 (C-4).
23	δ_H: 8.74 (1H, H–C=O); 6.28 (dd, 1H, H-6, J_{5-6}=5.5 Hz, J_{7-6}=3.0 Hz); 6.17 (dd, 1H, H-5, J_{6-5}=5.5 Hz, J_{4-5}=3.1 Hz); 4.54 (br., 1H, H-7a); 3.55 (br., 1H, H-7); 3.49 (d mult., 1H, H-3a, J_{7a-3a}=8.9 Hz); 3.27 (br., 1H, H-4); 1.66 (d mult., 1H, H-8a, J_{8b-8a}=10.0 Hz); 1.39 (d mult., 1H, H-8b, J_{8a-8b}=10.0 Hz). δ_F: +11.2 (CF_3-3). δ_C: 160.9 (C=O); 147.4 (q, C-3, ^2J=36.8 Hz); 138.7 (C-6); 136.4 (C-5); 119 (q, CF_3-3, ^1J=271.8 Hz); 65.6 (C-7a); 54.0 (C-7); 47.3 (C-3a); 45.9 (C-4); 42.5 (C-8).
24	δ_H: 8.18 (1H, N=CH); 3.20 (3H, CH_3). δ_F: +12.1 (CF_3-3). δ_C: 139.3 (HC=N); 30.8 (CH_3).

[a] Singlets unless stated otherwise.

[b] Aromatic ^{13}C absorptions masked by those of acenaphthylene.

[c] Pyran ring absorptions masked by those of other compounds present.

(h) With cyclopentadiene

A mixture of the dichloroazine **2** (4.00 g, 15.33 mmol) and freshly prepared cyclopentadiene (1.00 g, 15.20 mmol), shaken at room temperature (8 d), gave a −45 °C fraction identified as unchanged dichloroazine **2** (1.71 g, 6.55 mmol, 43% recovered) and a dark oily non-volatile residue (3.28 g) which was shown (^1H, ^{13}C, ^{19}F NMR and mass spectroscopy) to contain a major product identified as 1-(1,1-dichloro-2,2,2-trifluoroethyl)-3-trifluoromethyl-3a,6a-dihydro-1*H*,4*H*-cyclopenta[1,2-*c*]pyrazole (**3b**) (nc) (Analysis: Found: M^+, 326/328/330. $C_9H_6Cl_2F_6N_2$ requires: M, 327), a minor product identified as a mixture of 1-(1,1-dichloro-2,2,2-trifluoroethyl)-3-trifluoromethyl-3a,4,4a,7a,8,8a-hexahydro-4,8-methano-1*H*,5*H*-cyclopenta[1,2-*f*]indazole (**3j**) and its 1*H*,7*H* isomer (**3k**) by a comparison of the spectral data obtained with those of the same mixture formed by the reaction of dichloroazine **2** with dicyclopentadiene.

The residue on passage through a DCFC column (eluant: light petroleum/$CHCl_3$ 8:5 v/v) gave the following compounds: (i) a thick liquid (1.87 g) which was further purified by preparative-scale TLC (same eluant) to afford 1-trifluoroacetyl-3-trifluoromethyl-3a,6a-dihydro-1*H*,4*H*-cyclopenta[1,2-*c*]pyrazole (**4b**) (nc) (1.68 g, 6.18 mmol, 71%) (Analysis: Found: C, 39.7; H, 2.2; N, 10.6; F, 41.7%; M^+, 272. $C_9H_6F_6N_2O$ requires: C, 39.7; H, 2.2; N, 10.3; F, 41.9%; M, 272); (ii) a thick liquid (0.24 g) which was further purified by preparative-scale TLC (eluant: light petroleum/$CHCl_3$ 1:1 v/v) to give a mixture of 1-trifluoroacetyl-3-

Table 4
Mass spectral data

Compound	MS [a], m/z [b] (%, assignment) [c]
3a	328 (9, M^+); 259 [6, $(M-CF_3)^+$]; 242 [38, $(M-C_5H_7F)^+$]; 224 [14 $(M-CF_3-Cl)^+$]; 220 (11, $C_8H_4ClF_3N_2^+$); 196 (18, $C_6H_4ClF_3N_2^+$); 177 [63, $(M-CF_3CCl_2)^+$]; 162 (66, $C_6H_5F_3N_2^+$); 161 (100, $C_6H_4F_3N_2^+$); 123 (15, $C_3H_2F_3N_2^+$); 105 (100, $C_6H_5N_2^+$); 91 (54, $C_6H_5N^+$); 77 (68, $C_6H_5^+$); 69 (26, CF_3^+); 67 (52, $C_5H_7^+$); 65 (13, $C_5H_5^+$); 41 (20, $C_3H_5^+$); 39 (15, $C_3H_3^+$).
3b	326 (5, M^+); 291 [100 $(M-Cl)^+$]; 257 [5, $(M-CF_3)^+$]; 255 [13, $(M-HCl_2)^+$]; 225 (4, $C_4ClF_6N_2$); 175 [3, $(M-CF_3CCl_2]^+$]; 160 (14, $C_6H_3F_3N_2^+$); 147 (6, $C_7H_6F_3^+$); 127 (30, $C_7H_5F_2^+$); 69 (36); 66 (52, $C_5H_6^+$).
3c [d]	356 (84, M^+).
3d	376 (8, M^+); 341 [12, $(M-Cl)^+$]; 210 (13, $C_{11}H_7F_3N^+$); 141 (11, $C_{10}H_7N^+$); 128 (14, $C_{10}H_8^+$); 117 (77, $C_9H_9^+$); 115 (100, $C_9H_7^+$); 76 (20, $C_6H_4^+$); 69 (80); 65 (13, $C_4H_3N^+/C_5H_5^+$); 63 (34, $C_5H_3^+$); 50 (40, CF_2^+); 53 (44, $C_4H_5^+$); 38 (25, C_2N^+).
3e [d]	412 (76, M^+).
3f	330 (5, M^+); 311 [23, $(M-F)^+$]; 299 [15, $(M-CH_2OH)^+$]; 295 [10, $(M-Cl)^+$]; 279 (8, $C_8H_6ClF_6N_2^+$); 195 (8, $C_6H_3ClF_3N_2^+$); 162 (13, $C_6H_5F_3N_2^+$); 149 (55, $C_5H_4F_3N_2^+$); 71 (49, $C_4H_7O^+$); 69 (100); 51 (27, $C_4H_3^+$); 38 (41).
3g [d]	344 (88, M^+).
3h/3i	353 (1, M^+); 317 [6, $(M-Cl)^+$]; 251 (4, $C_6H_2ClF_6N_2^+$); 216 (16, $C_6H_2F_6N_2^+$); 147 (3, $C_5H_2F_3N_2^+$); 91 (17, $C_7H_7^+$); 77 (6, $C_4HN_2^+$); 69 (22); 66 (100, $C_5H_6^+$); 65 (29, $C_5H_5^+$); 40 (26, $C_3H_4^+$); 39 (34).
3j/3k	392 (6, M^+); 357 [57, $(M-Cl)^+$]; 356 [29, $(M-HCl)^+$]; 323 [98, $(M-CF_3)^+$]; 288 [100 $(M-CF_3\text{-}Cl)^+$]; 243 (16, $C_8H_5F_6N_2^+$); 216 (19, $C_{10}H_{11}F_3N_2^+$); 199 (19, $C_{10}H_8F_3N^+$); 69 (14); 52 (20, $C_4H_4^+$).
4a	274 (41, M^+); 255 [9, $(M-F)^+$]; 205 [25, $(M-CF_3)^+$]; 177 (25, $C_7H_8F_3N_2^+$); 161 (23, $C_7H_6F_3N^+$); 149 (17, $C_6H_6F_3N^+$); 97 (5, CF_3CO^+); 69 (100); 66 (31); 42 (76, CNO^+); 39(45); 28 (100, CO^+); 27 (28, $C_2H_3^+$).
4b	272 (82, M^+); 253 [8, $(M-F)^+$]; 203 [41, $(M-CF_3)^+$]; 177 [36, $(M-CF_3-C_2H_2)^+$]; 175 [35, $(M-CF_3CO)^+$]; 127 (68, $C_7H_5F_2^+$); 97 (6, CF_3CO^+); 80 (12, $C_5H_6N^+$); 77 (20, $C_6H_5^+$); 69 (100); 66 (47); 39 (50); 27 (23).
4c	302 (23, M^+); 246 [20, $(M-C_5H_8)^+$]; 245 [15, $(M-C_5H_9)^+$]; 233 [23, $(M-CF_3)^+$]; 205 [100, $(M-CF_3CO)^+$]; 149 (21, $C_5H_4F_3N_2^+$); 95 (34, CF_3CN^+); 94 (9, $C_7H_{10}^+$); 79 (13, $C_6H_7^+$); 69 (58); 55 (34); 42 (64, $C_3H_6^+/C_2H_4N^+$); 39 (24); 27 (14).
4d	322 (34, M^+); 253 [12, $(M-CF_3)^+$]; 227 [75, $(M-CF_3CN)^+$]; 177 (43, $C_6H_4F_3N_2O^+$); 140 (13, $C_{10}H_6N^+$); 128 (57, $C_9H_6N^+$); 116 (62, $C_9H_8^+$); 115 (27, $C_9H_7^+$); 91 (25, $C_7H_7^+$); 69 (59); 51 (20, $C_4H_3^+$); 40 (100, $C_2H_2N^+/C_3H_4^+$); 29 (52, CHO^+).
4e	358 (87, M^+); 289 [3, $(M-CF_3)^+$]; 263 [59, $(M-CF_3CN)^+$]; 239 [42, $(M-CF_3CON_2)^+$]; 194 (55, $C_{13}H_8NO^+$); 182 (10, $C_{12}H_8NO^+$); 166 (25, $C_{12}H_8N^+$); 164 (26, $C_{12}H_6N^+$); 152 (90, $C_{12}H_8^+$); 149 (19, $C_5H_4F_3N_2^+$); 86 (100, $C_7H_2^+$); 69 (24); 51 (20); 49 (48).
4f	276 (34, M^+); 257 [3, $(M-F)^+$]; 207 [25, $(M-CF_3)^+$]; 179 [10, $(M-CF_3CO)^+$]; 164 (16, $C_4F_3N_2O^+$); 149 (14, $C_6H_3N_2O^+$); 119 (8, $C_6H_3N_2^+$); 103 (22, $C_2F_3N^+$); 83 (9, $C_4H_5NO^+$); 77 (12, $C_4HN_2^+$); 70 (44, $C_4H_6O^+$); 69 (100, $CF_3^+/C_4H_5O^+$); 42 (25, $C_2H_2O^+$); 39 (19); 29 (32); 27 (18).
4g	290 (3, M^+); 271 [1, $(M-F)^+$]; 221 [2, $(M-CF_3)^+$]; 195 [7, $(M-CF_3CN)^+$]; 176 [57, $(M-C_2F_4N)^+$]; 151 (16, $C_7H_7N_2O_2^+$); 149 (100, $C_4F_3N_2O^+$); 107 (12, $C_3F_3N^+$); 85 (85, $C_5H_9O^+$); 69 (84); 55 (17, $C_3H_3O^+$); 53 (12, $C_4H_5^+$); 43 (17, $C_2H_3O^+$); 41 (30); 31 (16, CF^+); 29 (36); 27 (31).
4h	298 (2, M^+); 232 [3, $(M-C_5H_6)^+$]; 213 [5, $(M-C_5H_6-F)^+$]; 185 (4, $C_9H_6F_3N^+$); 163 (3, $C_5H_2F_3N_2O^+$); 69 (36); 66 (100, $C_5H_6^+$); 65 (21); 50 (5, CF_2^+); 40 (25); 39(27); 27 (10).
4i [e]	299 [13, $(M+H)^+$]; 298 (8, M^+); 273 [2, $(M+H-C_2H_2)^+$]; 210 [38, $(M-CF_4)^+$]; 52 (100, $C_4H_4^+$).
4j/4k	338 (14, M^+); 269 [2, $(M-CF_3)^+$]; 226 (12, $C_{12}H_{11}F_3N^+$); 156 (5, $C_{11}H_{10}N^+$); 131 (5, $C_{10}H_{11}^+$); 105 (41, $C_6H_5N_2^+/C_8H_9^+$); 91 (73, $C_6H_5N^+$); 78 (56, $C_5H_4N^+$); 69 (58); 66 (100); 53 (12); 40 (13); 27 (31).
5	308 (5, M^+); 273 [3, $(M-Cl)^+$]; 212 (9, $C_6HClF_4N_2^+$); 157 (10, $C_3HClF_3N_2^+$); 150 (6, $C_5H_3F_3NO^+$); 108 (13, $C_6H_6NO^+$); 82 (7, $C_5H_6O^+$); 69 (100); 67 (27, $C_4H_3O^+$); 55 (23, $C_3H_3O^+$); 43 (25, $C_2H_3O^+$); 39 (19); 31 (16).
6	180 (8, M^+); 179 [28, $(M-H)^+$]; 167 [6, $(M-CH)^+$]; 153 [22, $(M-C_2H_3)^+$]; 152 [14, $(M-C_2H_4)^+$]; 151 [29, $(M-CHO)^+$]; 83 (32, $C_5H_7O^+$); 69 (100); 55 (67); 53 (29); 43 (45); 41 (43); 29 (30).
7	230 (9, M^+); 195 [6 $(M-Cl)^+$]; 185 [13, $(M-CH_2OH)^+$]; 172 [78, $(M-C_3H_6O)^+$]; 159 [5, $(M-CF_3)^+$]; 145 [6, $(M-C_5H_9O)^+$]; 139 (41, $C_4H_6F_3N_2^+$); 111 (22, $C_5H_7N_2O^+$); 85 (80, $C_5H_9O^+$); 69 (60); 57 (100, $C_3H_5O^+$); 43 (87); 29 (83); 27 (37).
8 [e]	212 [76, $(M+NH_4)^+$]; 195 [100, $(M+H)^+$]; 194 (1, M^+); 144 (5, $C_7H_8F_2N^+$); 107 (17, $C_6H_5NO^+$); 69 (10); 52 (20, $C_2N_2^+$); 31 (19); 27 (13).
9	362 (100, M^+); 343 [8, $(M-F)^+$]; 296 [23, $(M-C_5H_6)^+$]; 293 [6, $(M-CF_3)^+$]; 277 [16, $(M-C_5H_6-F)^+$]; 230 [3, $(M-2C_5H_6)^+$]; 227 [19, $(M-C_5H_6-CF_3)^+$]; 211 [2, $(M-2C_5H_6-F)^+$]; 204 (9, $C_6H_2F_6O^+$); 92 (22, $C_7H_8^+$); 69 (10); 66 (71, $C_5H_6^+$).
21a	226 (96, M^+); 225 [21, $(M-H)^+$]; 212 [15, $(M-CH_2)^+$]; 207 $(M-F)^+$]; 177 [31, $(M-H_2FN_2)^+$]; 157 [52, $(M-CF_3)^+$]; 145 [32, $(M-C_2F_3)^+$]; 143 [34, $(M-CF_3N)^+$]; 130 [84, $(M-C_2HF_3N)^+$]; 115 (100, $C_9H_7^+$); 103 (40, $C_8H_7^+$); 77 (45, $C_6H_5^+$); 69 (31); 50 (29); 39 (28).
21b/21c	202 (6, M^+); 201 [12, $(M-H)^+$]; 189 [6, $(M-CH)^+$]; 183 [9, $(M-F)^+$]; 177 [88, $(M-C_2H)^+$]; 176 [140, $(M-C_2H_2)^+$]; 136 [96, $(M-C_5H_6)^+$]; 117 (75, $C_8H_7N^+$); 69 (30); 67 (82, $C_5H_7^+$); 66 (93, $C_5H_6^+$); 65 (87, $C_5H_5^+$); 40 (42); 39 (100, $C_3H_3^+$).
23	230 (11, M^+); 201 [1, $(M-CHO)^+$]; 135 [5, $(M-CF_3CN)^+$]; 117 (7); 79 (6, C_4HNO^+); 66 (100); 40 (15); 39 (25); 29 (11, CHO^+).
24 [d]	243 (100, M^+); 215 [64, $(M-CH_2N)^+$]; 177 [82, $(M-C_5H_6)^+$].

[a] EI spectra unless stated otherwise.
[b] For ions containing chlorine only the ^{35}Cl isotope peak is given.
[c] Expressed as percentage of base peak.
[d] FAB spectra.
[e] CI spectra.

trifluoromethyl-3a,4,4a,7a,8,8a-hexahydro-1*H*,5*H*-cyclopenta[1,2-*f*]indazole (**4j**) and its 1*H*,7*H* isomer (**4k**) (0.16 g, 0.47 mmol, 5%), identified by a comparison of the IR, NMR and mass spectra with those of the same mixture of compounds prepared by reaction of the dichloroazine **2** with dicyclopentadiene; and (iii) dicyclopentadiene (0.46 g, 3.48 mmol, 46%).

(*i*) *With dicyclopentadiene*

A mixture of dichloroazine **2** (4.00 g, 15.33 mmol) and dicyclopentadiene (2.02 g, 15.30 mmol), heated at 35–40 °C (16 d), gave volatile material (-45 °C fraction) identified as unchanged dichloroazine **2** (1.26 g, 4.83 mmol, 32% recovered) and a dark brown non-volatile residue (3.86 g) which was shown (^{1}H and ^{19}F NMR and mass spectroscopy) to consist of two major products (ratio 1:1) together with unchanged dicyclopentadiene and several minor components. The two major products were identified as the isomers 1-(1,1-dichloro-2,2,2-trifluoroethyl)-3-trifluoromethyl-3a,4,4a,7a,8,8a-hexahydro-4,8-methano-1*H*,5*H*-cyclopenta-[1,2-*f*]indazole (**3j**) (nc) and 1-(1,1-dichloro-2,2,2-trifluoroethyl)-3-trifluoromethyl-3a,4,4a,7a,8,8a-hexahydro-4,8-methano-1*H*,7*H*-cyclopenta[1,2-*f*]indazole (**3k**) (nc) (Analysis: Found: M^+, 392/394/396. $C_{14}H_{12}Cl_2F_6N_2$ requires: M, 393).

The residue on passage through a DCFC column (eluant: light petroleum/CH_2Cl_2 2:1 v/v) gave (i) unchanged dicyclopentadiene (0.62 g, 4.67 mmol, 31% recovered) and (ii) a mixture of the two isomers (1:1 molar ratio) 1-trifluoroacetyl-3-trifluoromethyl-3a,4,4a,7a,8,8a-hexahydro-4,8-methano-1*H*,5*H*-cyclopenta[1,2-*f*]indazole (**4j**) (nc) and 1-trifluoroacetyl-3-trifluoromethyl-3a,4,4a,7a,8,8a-hexahydro-4,8-methano-1*H*,7*H*-cyclopenta[1,2-*f*]indazole (**4k**) (nc) (2.68 g, 7.93 mmol, 76%) (Analysis: Found: C, 50.0; H, 3.9; N, 8.1%; M^+, 338. $C_{14}H_{12}F_6N_2O$ requires: C, 49.7; H, 3.6; N, 8.3%; M, 338).

3.4. Hydrolysis of 1-trifluoroacetyl-3-trifluoromethyl-3a,5,6,7a-tetrahydro-1H,4H-pyrano[2,3-c]pyrazole (4g)

A mixture of the pyrazole **4g** (0.40 g, 1.38 mmol) and silica gel (2.0 g) in diethyl ether (ca. 25 cm^3) was poured on to the top of a DCFC column and left for 4 h before elution with dichloromethane. This gave a solid product which was washed with ethanol-free chloroform (2×3 cm^3) to afford 5-[1-(2,2,2-trifluoroethylidenehydrazono)]-3,4-dihydro-2*H*-pyran (**8**) (0.24 g, 1.24 mmol, 93%).

3.5. Reaction of 1-trifluoroacetyl-3-trifluoromethyl-3a,8b-dihydro-1H,4H-indeno[1,2-c]pyrazole (4d) with methylamine

A solution of methylamine (3.0 g, 31.9 mmol, 33% w/w in EtOH) in diethyl ether (5 cm^3) was added in one portion to a stirred solution of the pyrazole **4d** (1.00 g, 3.11 mmol) in diethyl ether (25 cm^3), and stirring was continued (0.5 h). Removal of the solvent under reduced pressure gave a mixture (1.02 g) of *N*-methyltrifluoroacetamide (**22**) and a second component. Separation of the mixture by DCFC (eluant: light petroleum/CH_2Cl_2 1:1 v/v) gave 3-trifluoromethyl-3a,8b-dihydro-1*H*,4*H*-indeno[1,2-*c*]pyrazole (**21a**) (nc) (0.66 g, 2.92 mmol, 94%) (Analysis: Found: M^+, 226.0702. $C_{11}H_9F_3N_2$ requires: M, 226.0718) and *N*-methyltrifluoroacetamide (**19**) (0.36 g, 2.83 mmol, 91%).

3.6. Reaction of 1-trifluoroacetyl-3-trifluoromethyl-3a,4,7,7a-tetrahydro-4,7-methano-1H-indazole (4h) with methylamine

(a) Experiment 1

A solution of methylamine (3.0 g, 31.9 mmol, 33% w/w in EtOH) in diethyl ether (5 cm^3) was added in one portion to a stirred solution of the *exo*-indazole **4h** (0.40 g, 1.34 mmol) in diethyl ether (15 cm^3), and stirring was continued (0.5 h). Removal of the solvent under reduced pressure gave a residue which was purified by preparative-scale TLC (eluant: CH_2Cl_2) to afford 1-formyl 3-trifluoromethyl-3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indazole (**23**) (nc) (0.27 g, 1.17 mmol, 87%) (Analysis: Found: M, 231.0741. $C_{10}H_9F_3N_2O$ requires: M, 231.0745).

(b) Experiment 2

A second experiment was carried out using methylamine (2.0 g, 21.3 mmol) and a mixture of the *exo* and *endo*-indazoles **4h** and **4j** (0.25 g, 0.84 mmol) in the ratio 1:1.1 in diethyl ether (20 cm^3). After stirring (0.5 h), the solvent was removed under reduced pressure and a TLC examination (eluant: light petroleum/CH_2Cl_2 1:1 v/v) showed the presence of three components; compound **23** was absent.

The major product was separated by preparative-scale TLC (same eluant) and was identified as a mixture of *exo*- and *endo*-3-trifluoromethyl-3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indazole (**21b**) (nc) and (**21c**) (nc) (0.15 g, 0.74 mmol, 88%) [Analysis: Found: $(M+H)^+$, 203.0799. $C_9H_{10}F_3N_2$ requires: M+1, 203.0796].

A second fraction (0.021 g) was obtained, which was shown (NMR spectroscopy) to consist of *N*-methyltrifluoroacetamide (**22**) (ca. 0.011 g, ca. 0.087 mmol, ca. 10%) and 1-(2-azaprop-1-en-1-yl)-3-trifluoromethyl-3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indazole (**24**) (nc) (ca. 0.01 g, ca. 0.04 mmol, ca. 5%) (Analysis: Found: M^+, 243.1013. $C_{11}H_{12}F_3N$ requires: M, 243.0983). This mixture hydrolysed on storage (5 h) and a ^{1}H NMR spectrum showed the absence of the azapropenylindazole **24** and the presence of the 1-formylindazole **23**.

The NMR and mass spectra of the new compounds **3–9**, **21**, **23** and **24** are summarised in Tables 3 and 4, respectively.

Acknowledgements

We thank the Hariri Foundation for a grant (to M.M. A-G.) and Dr. M.G. Barlow (UMIST) for helpful discussions regarding the NMR spectra.

References

[1] M.G. Barlow, N.N.E. Suliman and A.E. Tipping, *J. Fluorine Chem., 72* (1995) 147.
[2] M.M. Abdul-Ghani and A.E. Tipping, *J. Fluorine Chem., 63* (1993) 5.
[3] K. Burger, W. Thenn and A. Gieren, *Angew. Chem., 86* (1974) 481; A. Gieren, P. Narayanan, K. Burger and W. Thenn, *Angew. Chem., 86* (1974) 482.
[4] T.P. Forshaw and A.E. Tipping, *J. Chem. Soc. C,* (1971) 2402; S.E. Armstrong and A.E. Tipping, *J. Chem. Soc., Perkin Trans. 1,* (1975) 538, 1411.
[5] N.J. O'Reilly, *Ph.D. Thesis,* University of Manchester, 1984.
[6] J. Plenkiewicz, *Bull. Acad. Pol. Sci., Ser. Sci. Chim., 25* (1977) 19.
[7] S. Wolfgang, US Pat. 4 168 282, 1978.
[8] W. Boland and L. Jaenicke, *Chem. Ber., 111* (1978) 3262.
[9] K. Burger and F. Hein, *Liebigs Ann. Chem.,* (1982) 853.
[10] F. Weygand and E. Frauendorfer, *Chem. Ber., 103* (1970) 2437.
[11] M.G. Barlow, D. Bell (in part), N.J. O'Reilly and A.E. Tipping, *J. Fluorine Chem., 23* (1983) 293.
[12] D. Bell (in part), A.O.A. Eltoum (in part), N.J. O'Reilly and A.E. Tipping, *J. Fluorine Chem., 64* (1993) 151.