Unsaturated nitrogen compounds containing fluorine. Part 14 [1]. A re-investigation of the reaction of 2,5-dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene with triethylamine and some related reactions

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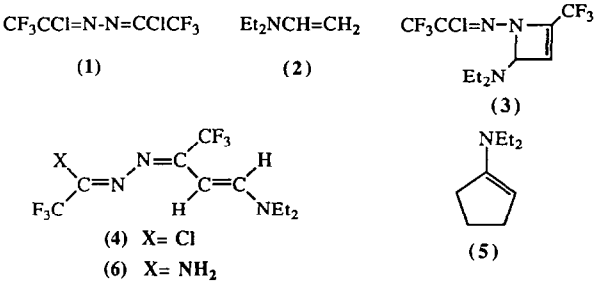
Abstract

The reaction of triethylamine with the title azine **1** (2:1 molar ratio) in light gives, as the major product, an orange liquid considered previously to be the Δ^2-azetine $CF_3CCl{=}N{-}N{-}C(CF_3){=}CHCHNEt_2$ (**3**), but now shown to be the open-chain isomer, i.e. the triazadecatriene $CF_3CCl{=}NN{=}C(CF_3)CH{=}CHNEt_2$ (**4**) by a comparison of its ^1H, ^{13}C and ^{19}F NMR spectra with those of its solid amino derivative $CF_3C(NH_2){=}NN{=}C(CF_3)CH{=}CHNEt_2$ (**6**) (made in 96% yield by reaction of compound **4** with ammonia) the structure of which has been established by X-ray crystallography. A second reaction using a large excess of triethylamine (6:1 molar ratio in light followed by heating at 115 °C) affords compound **4** (17%), its diethylamino derivative $CF_3C(NEt_2){-}NN{=}C(CF_3)CH{=}CHNEt_2$ (**8**) (12%), the tetra-azatetradecatetraene $Et_2NCH{=}CHC(CF_3){=}NN{=}C(CF_3)CH{=}CHNEt_2$ (**9**) (6%) and the hydrolysis product of compound **9**, the dienol $N{=}C(CF_3)CH_2CHNC(CF_3){=}CHCH(OH)O$ (**10**) (2%). Treatment of compound **9** with silica gel gives the dienol **10** (84%). The reaction of the triazadecatriene **4** with 1-diethylaminocyclopentene (**5**) (1:2 molar ratio) affords the 2-substituted enamine $CH_2(CH_2)_2C(NEt_2){=}C{-}C(CF_3){=}NN{=}C(CF_3)CH{=}CHNEt_2$ (**17**) (74%) and this on hydrolysis (silica gel) gives the corresponding 2-substituted ketone $O{=}C(CH_2)_3CHC(CF_3){=}NN{=}C(CF_3)CH{=}CHNEt_2$ (**18**) (75%) and the pyrazole derivative $O{=}C(CH_2)_3C{=}C(CF_3)NN{=}C(CF_3)CH{=}CH$ (**19**) (15%).

Introduction

It has been reported that the reaction between triethylamine and the dichloroazine **1** (2:1 molar ratio) in light (reaction did not occur in the dark) involved the intermediacy of the enamine $Et_2NCH{=}CH_2$ (**2**) and gave a major liquid product considered to be the Δ^2-azetine **3** (40%) on the basis of the spectral data obtained [2], although the ^1H NMR coupling ($J = 13$ Hz) between the two vicinal hydrogens in the azetine ring was much larger than expected. The dihedral angle α between the vicinal hydrogens has been estimated to be *c.* 70.5° by a computer enhanced modelling program (MOPAC 6.0 using a Textronix Cache Workstation) for which a much lower coupling constant ($J = 2$–6 Hz) would be appropriate. The only other possible structure based on the NMR data is the open-chain isomer of the azetine **3**, i.e. the triazadecatriene **4** with two *trans*-vinylic hydrogens (expected $J = 11$–18 Hz).

To resolve the problem of whether the product has structure **3** or **4**, the reaction has been repeated with the object of preparing a solid derivative on which an X-ray crystallographic structure determination could be undertaken. The reaction of a large excess of triethylamine with dichloroazine **1** has also been carried out with the object of synthesising a bis-enamine derivative and the reaction of the enamine 1-diethylaminocyclopentene (**5**) with compound **3** or **4** has been investigated.



Results and discussion

Reaction of triethylamine with dichloroazine **1** (2:1 molar ratio) *in vacuo* in light at room temperature (7 d) gave unchanged triethylamine (14% recovered), trifluoroacetonitrile (6%), impure triethylamine hydro-

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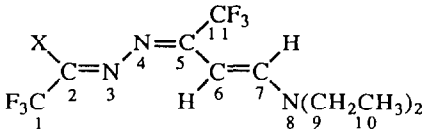
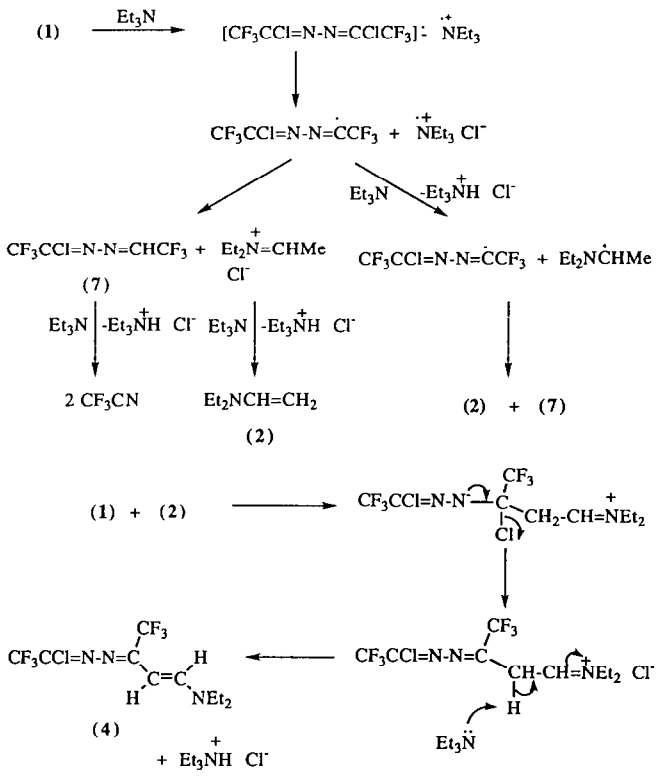
TABLE 1. NMR spectra of 2-substituted-8-ethyl-1,1,1-trifluoro-5-trifluoromethyl-3,4,8-triazadeca-2,4,6-trienes **4**, **6**, **8**, **9**, **17** and **18**



Compound	Spectrum	δ/ppm (assignment)
4[a]	^{1}H	7.4 (d, 1H, H-7, $J_{6,7}$=13 Hz); 5.0 (d, 1H, H-6, $J_{7,6}$=13 Hz); 3.3 (q, 4H, H-9/9′, J=7 Hz); 1.2 (t, 6H, H-10/10′, J=7 Hz).
6[b]		7.88 (d, 1H, H-7, $J_{6,7}$=13.9 Hz); 5.39 (d, 1H, H-6, $J_{7,6}$=13.9 Hz); 3.45 (q, 4H, H-9/9′, J=7.0 Hz); 1.38 (t, 6H, H-10/10′, J=7.0 Hz).
8[c]		7.64 (d, 1H, H-7, $J_{6,7}$=13.0 Hz); 5.10 (d, 1H, H-6, $J_{7,6}$=13.0 Hz); 3.43 (q, 4H, H-9/9′, J=7.0 Hz); 1.20 (t, 6H, H-10/10′, J=7.0 Hz).
9[d]		7.75 (d, 1H, H-7, $J_{6,7}$=13.0 Hz); 4.98 (d, 1H, H-6, $J_{7,6}$=13.0 Hz); 3.19 (q, 4H, H-9/9′, J=7.0 Hz); 1.16 (t, 6H, H-10/10′, J=7.0 Hz).
17[e]		7.41 (d, 1H, H-7, $J_{6,7}$=13.5 Hz); 4.97 (d, 1H, H-6, $J_{7,6}$=13.5 Hz); 3.23 (q, 4H, H-9/9′, J=7.2 Hz); 1.16 (t, 6H, H-10/10′, J=7.2 Hz).
18[f]		7.47 (d, 1H, H-7, $J_{6,7}$=13.0 Hz); 5.00 (d, 1H, H-6, $J_{7,6}$=13.0 Hz); 3.28 (q, 4H, H-9/9′, J=7.0 Hz); 1.22 (t, 6H, H-10/10′, J=7.0 Hz).
4[a]	^{19}F	9.0 (s, 3F, CF_3-1); 12.0 (s, 3F, CF_3-11).
6[b]		7.1 (s, 3F, CF_3-1); 12.0 (s, 3F, CF_3-11).
8[c]		14.2 (s, 3F, CF_3-1); 11.7 (s, 3F, CF_3-11).
9[d]		10.4 (s, CF_3-1/11).
17[e]		8.9 (s, 3F, CF_3-1); 11.1 (s, 3F, CF_3-11).
18[f]		9.0 (s, 3F, CF_3-1); 11.1 (s, 3F, CF_3-11).
4[a]	^{13}C	152.9 (q, C-5, ^2J=30.7 Hz); 151.6 (s, C-7); 130.0 (q, C-2, ^2J=40.1 Hz); 121.1 (q, C-11, ^1J=277.4 Hz); 117.8 (q, C-1, ^1J=273.9 Hz); 83.3 (s, C-6); 51.2 and 42.3 (2s, C-9/9′); 14.5 and 11.1 (2s, C-10/10′).
6[b]		152.2 (q, C-5, ^2J=29.4 Hz); 149.9 (s, C-7); 146.5 (q, C-2, ^2J=34.5 Hz); 121.7 (q, C-11, ^2J=277.2 Hz); 118.9 (q, C-1, ^1J=274.7 Hz); 83.4 (s, C-6); 50.3 and 41.7 (2s, C-9/9′); 14.3 and 11.6 (2s, C-10/10′).
8[c]		149.2 (s, C-7); 148.1 (q, C-5, ^2J=29.5 Hz); 143.3 (q, C-2, ^2J=30.2 Hz); 122.0 (q, C-11, ^1J=276.7 Hz); 119.9 (q, C-1, ^1J=278.4 Hz); 83.5 (s, C-6); 45.3 (s, C-9/9′); 14.1 (s, C-10/10′).
9[d]		150.1 (s, C-7); 147.9 (q, C-2/5, ^2J=29.4 Hz); 122.0 (q, C-1/11, ^1J=276.8 Hz); 83.3 (s, C-6); 49.4 and 42.8 (2s, C-9/9′); 12.9 (s, C-10/10′).
17[e]		151.3 (q, C-5, ^2J=30.5 Hz); 149.7 (s, C-7); 147.6 (q, C-2, ^2J=30.2 Hz); 121.8 (q, C-1, ^1J=278.0 Hz); 121.6 (q, C-11, ^1J=276.9 Hz); 84.0 (s, C-6); 44.7 (s, C-9/9′); 13.3 (s, C-10/10′).
18[f]		153.1 (s, C-7); 150.4 (q, C-5, ^2J=30.2 Hz); 146.8 (q, C-2, ^2J=32.5 Hz); 121.4 (q, C-11, ^1J=277.3 Hz); 120.8 (q, C-1, ^1J=274.7 Hz); 83.8 (s, C-6); 50.8 and 42.3 (2s, C-9/9′); 14.2 and 11.4 (2s, C-10/10′).

[a]X = Cl.
[b]X = NH_2 [^{1}H NMR δ: 5.46 (br., 2H, NH_2) ppm.].
[c]X = $N(CH_2CH_3)_2$ [^{1}H NMR δ: 3.32 (q, 4H, $2CH_2N$, J=7.0 Hz); and 1.20 (t, 6H, $2CH_3$, J=7.0 Hz) ppm. ^{13}C NMR δ: 45.3 (s, $2CH_2N$); and 14.1 (s, $2CH_3$) ppm].
[d]X = (*E*)-CH=CHNEt$_2$.
[e]X = $-\overline{C=C(NEt_2)CH_2CH_2CH_2}$ [^{1}H NMR δ: 2.89 (q, 4H, $2CH_2N$, J=7.0 Hz); 2.58 (t, 2H, ring CH_2, J=7.5 Hz); 2.54 (t, 2H, ring CH_2, J=7.5 Hz); 1.83 (pentet, 2H, ring $CH_2CH_2CH_2$, J=7.5 Hz); and 0.97 (t, 6H, $2CH_3$, J=7.0 Hz) ppm. ^{13}C NMR δ: 157.5 (s, ring =C−N); 94.2 (s, ring =*C*−C); 44.7 (s, $2CH_2N$); 35.2 and 33.3 (2s, 2 ring CH_2−C=); 21.3 (s, ring $CH_2CH_2CH_2$); and 13.3 (s, $2CH_3$) ppm].
[f]X = $-\overline{CHCH_2CH_2CH_2C}$=O [^{1}H NMR δ: 3.26 (mult., 1H, ring CH); and 2.50, 2.36–2.18 and 1.84 (3 mult., 1H, 4H and 1H, 3 ring CH_2) ppm. ^{13}C NMR δ: 213.2 (s, C=O); 48.8 (s, ring CH); 37.2 (s, ring CH_2C=O); and 27.1 and 21.9 (2s, 2 ring CH_2) ppm].

chloride, compound **3** or **4** (43%) and tar. Treatment of the product **3** or **4** with an excess of aqueous ammonia (*c.* 1 d) afforded a solid amino derivative (96%) which was shown to be the open-chain triazadeca-2(*Z*),4(*E*),6(*E*)-triene (**6**) by a single crystal X-ray structure determination [3].



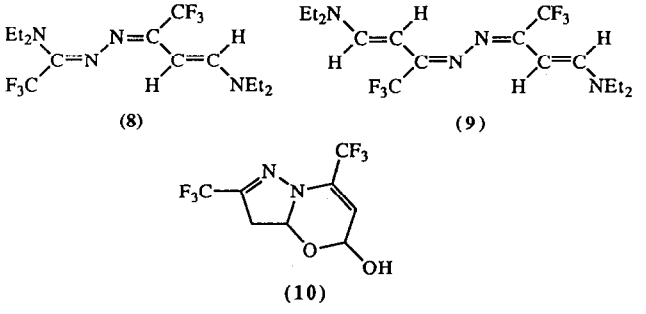
Scheme 1.

The ^1H NMR spectrum of compound **6** showed a *trans* coupling ($J = 13.9$ Hz) for the two vinylic hydrogens, which was of the same magnitude as that observed ($J = 13$ Hz) in the spectrum of compound **3** or **4**. Furthermore, the ^1H, ^{19}F and ^{13}C NMR spectra (Table 1) of the two compounds were virtually identical with due allowance made for the replacement of Cl by NH_2, thus establishing that the product isolated from the reaction of triethylamine with dichloroazine **1** is the open-chain triazadeca-2(*Z*),4(*E*),6(*E*)-triene (**4**) and not the Δ^2-azetine **3**.

Compound **4** is considered to have been formed by a single-electron transfer (SET) mechanism, as postulated previously [2], to afford as initial products, trifluoroacetonitrile, triethylamine hydrochloride and the enamine **2**. Nucleophilic attack on unchanged dichloroazine **1** then yielded compound **4** and hydrogen chloride which was isolated as triethylamine hydrochloride (Scheme 1).

Evidence has been advanced [4] for the intermediacy of the radical $Et_2\dot{N}CHMe$ as a precursor to enamine **2** in the photoreaction of ketones with triethylamine and an SET mechanism was proposed for the reduction of the *ortho*-quinone, β-lapachone, with triethylamine induced by visible light and involving the radical cation $Et_3\dot{N}^+$ as a precursor to the radical $Et_2\dot{N}CHMe$ and hence the enamine **2** [5].

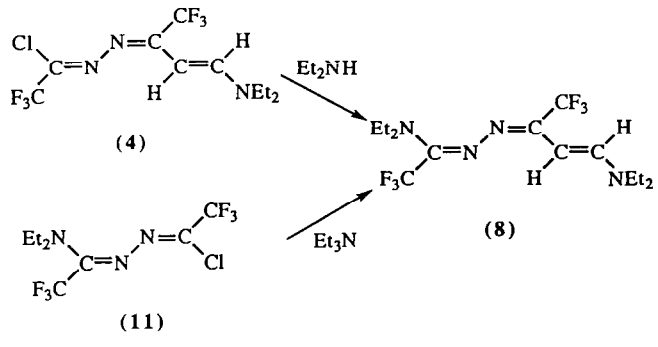
Reaction of a large excess of triethylamine with dichloroazine **1** (6:1 molar ratio) *in vacuo* in light at room temperature (7 d) gave mainly compound **4** (TLC) and so the reactants were resealed in the ampoule and heated at 115 °C (14 d) to afford unchanged triethylamine (53.5% recovered), triethylamine hydrochloride (61% on Et_3N used; 86% on azine **1**), a higher boiling mixture from which the four major components, i.e. compound **4** (17%), the diethylamino-substituted triene **8** (12%), the tetra-azatetraene **9** (6%) and the bicyclic dienol **10** (2%) were separated, and tar. The dienol **10** was formed by hydrolysis of the tetra-azatetraene **9** as shown by exposing the tetraene **9** to silica gel (1 d) which gave the dienol **10** (84%).



Compound **8** (then presumed to be the isomeric diethylamino-substituted Δ^2-azetine) has been made previously (i) by reaction of the monochloroazine **11** with triethylamine at 130 °C (7 d) in 75% yield and (ii) by reaction of compound **4** (thought to be the Δ^2-azetine **3**) with diethylamine (1:2 molar ratio) in diethyl ether at room temperature in 88% yield [2] (Scheme 2).

The IR, ^1H, ^{13}C and ^{19}F NMR, and mass spectra of compound **8** were identical to those reported [2] and the ^1H, ^{13}C and ^{19}F NMR spectra were very similar to those of compounds **4** and **6** (Table 1).

Compound **9** is symmetrical about the N–N bond and NMR absorptions were only observed for one $Et_2NCH{=}CHC(CF_3){=}N-$ grouping; the absorptions were in agreement with the absorptions for the same grouping in compounds **4**, **6** and **8** (Table 1).



Scheme 2.

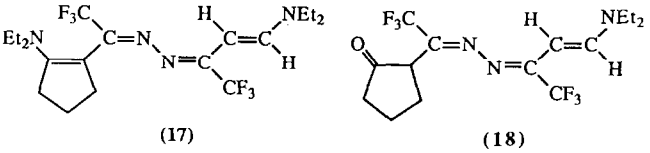
The dienol **10** gave correct elemental analysis figures (for C, H and N) and a molecular ion peak (*m/z*: 276) in its mass spectrum confirmed the molecular formula as $C_8H_6N_2OF_6$. The ^1H, H,H-COSY, ^{13}C and ^{19}F NMR spectra established the structure as follows. The vinylic proton [δ_H: 5.34 (dq, 1H, $J=3.2$ and 1.7 Hz) ppm. δ_C: 113.0 (q, $^3J=4.1$ Hz) ppm] in a $CF_3C=CH$ grouping was shown by a H,H-COSY spectrum to be coupling to a low-field non-vinylic proton [δ_H: 5.99 (dd, 1H, $J=3.2$ and 1.0 Hz) ppm. δ_C: 85.9 ppm] with the chemical shifts consistent with a $-CH(O)-O-$ grouping. This evidence, together with the presence of a hydroxyl proton [δ_H: 3.08 ppm, IR ($\nu_{max.}$) (cm^{-1}): 3380 (O–H str.)], gave the partial structure $CF_3\underset{|}{C}=CH-CH(OH)-O-$. A low-field methine proton [δ_H: 5.67 (dt, 1H, $J=7.4$ and 0.4 Hz) ppm. δ_C: 80.9 ppm] showed coupling to two non-equivalent methylene protons CH_AH_B [δ_H: 3.32 (ABdd, 1H, H_A, $J_{B,A}=18.0$ Hz, $J=7.4$ and 1.8 Hz) and 3.04 (ABdd, 1H, H_B, $J_{A,B}=18.0$ Hz, $J=1.0$ and 0.4 Hz) ppm], and the chemical shift of the methine proton was consistent with it being bonded to nitrogen and to oxygen. This indicated that the dienol contained the extended partial structure $CF_3\underset{|}{C}=CH-CH(OH)-O-CH(N-)-CH_AH_B-$. The ^{13}C NMR spectrum also showed the presence of two CF_3 carbons [δ_C: 119.9 (q, $^1J=273.7$ Hz) and 119.8 (q, $^1J=270.6$ Hz) ppm], a β-imino carbon $CF_3C=N$ [δ_C: 145.7 (q, $^2J=38.9$ Hz) ppm] and a β-vinylic carbon $CF_3C=C$ [δ_C: 131.9 (q, $^2J=36.4$ Hz) ppm]; the ^{19}F NMR spectrum confirmed the presence of two non-equivalent CF_3 groups (δ_F: +10.7 and +10.1 ppm). This gave the partial structure $CF_3\underset{|}{C}=N-\underset{|}{N}-C(CF_3)=$ based on the azine skeleton present in the tetraene **9** and, when combined with the extended partial structure above, established that the product was the dienol **10**.

Compounds **8**–**10** are considered to have been formed from the triene **4** as shown in Scheme 3.

Nucleophilic attack on the imino carbon of the $CF_3CCl=N-$ grouping in triene **4** by triethylamine gives the zwitterion **11** which, by a concerted loss of hydrogen chloride and ethene, affords the substituted triene **8**, while nucleophilic attack by enamine **2** followed by elimination of hydrogen chloride yields the tetra-azatetraene **9**.

Acid-catalysed hydrolysis of the tetraene **9** on silica gel involved initial formation of the mono-aldehyde **12** and then the dialdehyde **13** with concurrent elimination of diethylamine. Tautomerisation of the dialdehyde **13** to the conjugated endial **14** on acid catalysis, followed by cyclisation involving internal nucleophilic attack by nitrogen on the carbonyl carbon of the non-conjugated aldehyde group, leads to the alkoxide **15** which undergoes a second nucleophilic attack by oxygen on the carbonyl carbon of the remaining conjugated aldehyde group. The resulting intermediate **16** affords the dienol **10** by protonation/deprotonation.

Treatment of the triene **4** with the enamine **5** (1:2 molar ratio) in diethyl ether under a nitrogen atmosphere gave the 2-substituted enamine **17** (74%) and this on hydrolysis with silica gel afforded the corresponding 2-substituted cyclopentanone **18** (75%) and the bicyclic pyrazole **19** (15%).



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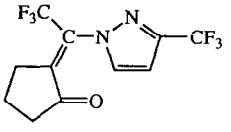


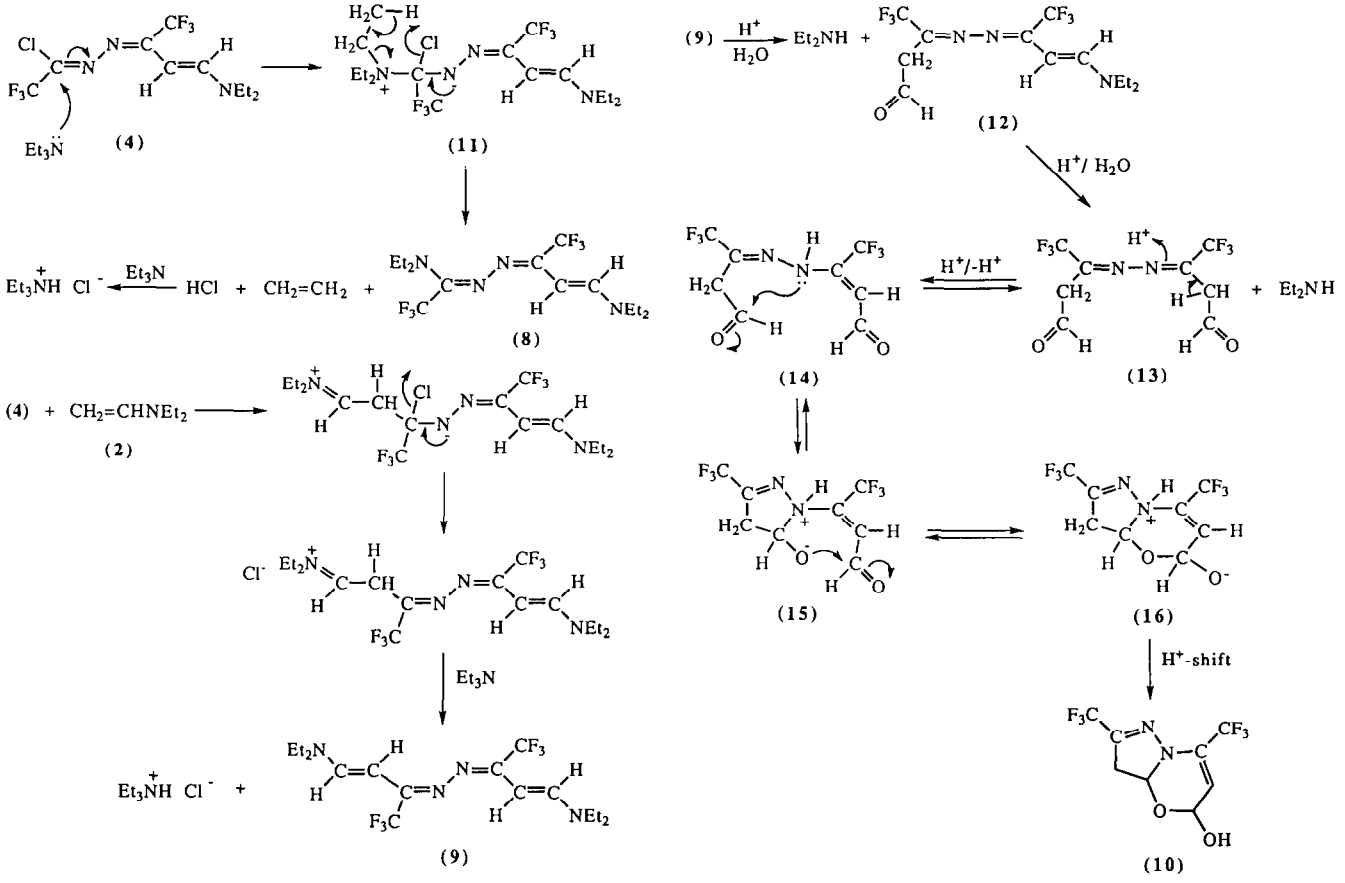
(19)

Compound **17** was formed analogously to the tetraene **9** by nucleophilic attack by the β-carbon of the enamine on the imino carbon of the $CF_3CCl=N-$ grouping in compound **4** followed by loss of hydrogen chloride. The isolation of the 2-substituted cyclopentanone **18** as the major hydrolysis product showed that the cyclic enamine grouping is hydrolysed more readily than the open-chain enamine grouping in compound **17**. Hydrolysis of the second enamine grouping in compound **18** to afford the onal **20**, followed by tautomerisation, cyclisation and then elimination of water gave the bicyclic pyrazole **19** (Scheme 4).

An accurate mass measurement on compound **17** and correct elemental analysis figures (for C, H and N) together with molecular ion peaks (*m/z*: 371 and 298, respectively) in the mass spectra of compounds **18** and **19** established the molecular formulae of the three compounds. Their structures were then established by the following spectral data.

Compounds **17** and **18** were clearly derivatives of the triene **4** as shown by a comparison of their NMR spectra with those of the compounds **4**, **6**, **8** and **9** and the substituent X was shown to be diethylaminocyclopenten-2-yl and cyclopentanon-2-yl, respectively, by the ^1H and ^{13}C NMR absorptions (Table 1).

For compound **19**, the presence of a 1-substituted 3-trifluoromethylpyrazole ring was shown by two coupled vinylic protons [^1H NMR δ: 7.48 (d, 1H, =CH–N, $J=2.8$ Hz) and 6.67 (d, 1H, =CH–C, $J=2.8$ Hz) ppm. ^{13}C NMR δ: 133.4 and 102.9 ppm] and a $CF_3C=N$ grouping [^{13}C NMR δ: 144.5 (q, $CF_3C=N$, $^2J=38.8$ Hz); and 120.7 (q, $CF_3C=N$, $^1J=268.6$ Hz) ppm. ^{19}F NMR δ: 16.4 (s) ppm]. A cyclopentanon-2-ylidine ring was also present as shown by a ketonic carbonyl group



Scheme 3.

(^{13}C NMR δ: 201.8 ppm), three coupled methylene groups [^{1}H NMR δ: 3.12 (tq, 2H, $CH_2CH_2C{=}$, J=7.5 Hz, J_{CF-CH}=3.0 Hz); 2.39 (t, 2H, $CH_2CH_2C{=}O$, J=7.5 Hz); and 2.06 (pentet, $CH_2CH_2CH_2$, J=7.5 Hz) ppm. ^{13}C NMR δ: 38.5 (s, $CH_2C{=}O$); 28.5 (q, $CH_2C{=}$, ^4J=2.3 Hz); and 18.5 (s, $CH_2CH_2CH_2$) ppm] and a vinylic carbon [^{13}C NMR δ: 141.8 (s) ppm] which was bonded to a $=C(CF_3)-N$ grouping [^{13}C NMR δ: 144.5 (q, $=C(CF_3)-N$, ^2J=45.1 Hz); and 120.4 (q, $=C(CF_3)-N$, ^1J=276.7 Hz) ppm. ^{19}F NMR δ: 13.6 (t, CF_3, J_{CH-CF}=3.0 Hz) ppm]. This evidence proved conclusively that the product was the pyrazole derivative **19**.

The coupling (J=3.0 Hz) observed between the CF_3 group in the $=C(CF_3)-N$ grouping and the hydrogens of the $CH_2C{=}$ methylene group indicated strongly that the carbonyl group is *anti* to the CF_3 group and it is possible that this isomer is favoured because of hydrogen bonding between the carbonyl oxygen and the vinylic proton adjacent to nitrogen in the pyrazole ring.

Experimental

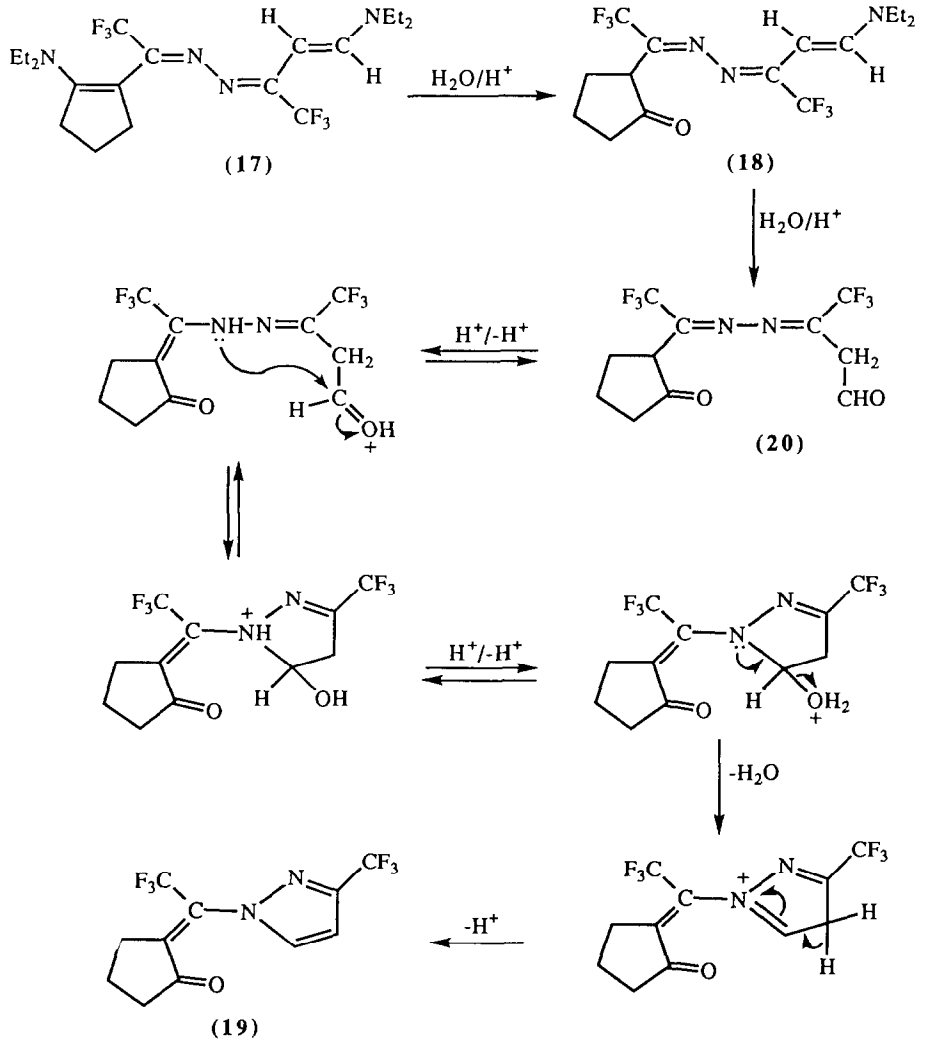
Starting materials

The dichloroazine **1** was synthesised in 60% yield by the reaction of trifluoroacetic acid with hydrazine (2:1 molar ratio) to give the bishydrazide CF_3CO-$NHNHCOCF_3$, followed by treatment with phosphoryl chloride and *N*,*N*-dimethylaniline hydrochloride [6], and 1-diethylaminocyclopentene (**5**) was prepared by treatment of diethylamine in diethyl ether with cyclopentanone and calcium chloride (12 mesh) [7]. Triethylamine was a commercial sample which was distilled and its purity checked (IR and ^{1}H NMR spectroscopy) before use.

General techniques

Products were examined by TLC (eluants as in text) and then purified where necessary, or the individual components of mixtures separated by dry column flash chromatography (DCFC) using silica gel (Fluka 60 GF_{254}) or neutral alumina (Brockmann 1, standard grade) and eluants as given in the text; the eluant referred to as light petroleum is the petroleum ether fraction, b.p. 30–40 °C.

Purified products and separated components were examined by IR spectroscopy (Perkin-Elmer DE783 instrument), ^{1}H NMR (including H,H-COSY) spectroscopy [Bruker AC300 (300 MHz) spectrometer; external reference Me_4Si], ^{19}F NMR spectroscopy [Bruker AC200 (188.3 MHz) instrument; external reference



Scheme 4.

CF_3CO_2H], ^{13}C NMR (including DEPT 135°) spectroscopy [Bruker AC300 (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 with an electron beam energy of 70 eV for low-resolution spectra and a Kratos Concept IS spectrometer for accurate mass measurement). The NMR spectra were run on solutions in $CDCl_3$ and chemical shifts to low field of reference are designated positive.

Boiling points were determined by Siwoloboff's method and melting points are uncorrected.

Reaction of 2,5-dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (1) with triethylamine

(a) Experiment 1 (1:2 molar ratio)

A mixture of the dichloroazine **1** (3.00 g, 11.49 mmol) and triethylamine (2.32 g, 22.99 mmol), shaken *in vacuo* in a Rotaflo ampoule (*c.* 50 cm^3) in light (7 d), gave (i) trifluoroacetonitrile (0.14 g, 1.47 mmol, 6%) which condensed at −196 °C, (ii) unchanged triethylamine (0.133 g, 3.27 mmol, 14% recovered) which condensed at −78 °C and −120 °C, and (iii) a residue which was washed out of the tube with diethyl ether (3×20 cm^3) and then filtered to give impure triethylamine hydrochloride (2.08 g, 15.13 mmol).

The filtrate was washed with water (2×25 cm^3), then with aqueous hydrochloric acid (2 M, 2×25 cm^3), dried ($MgSO_4$) and the diethyl ether removed *in vacuo* to afford an orange oil (2.33 g) which was shown by TLC (eluant: n-hexane/dichloromethane 2:1 v/v) to contain one major component (R_F 0.29) and several minor components. The major component was purified by DCFC (same eluant) to give 2-chloro-8-ethyl-1,1,1-trifluoro-5-trifluoromethyl-3,4,8-triazadeca-2,4,6-triene (**4**) (1.59 g, 4.92 mmol, 43%) which was identified by a comparison of its IR, ^1H, ^{13}C and ^{19}F NMR, and

mass spectra with those reported [2] and with those obtained for its amino derivative (see later).

(b) Experiment 2 (1:6 molar ratio)

A mixture of the dichloroazine **1** (4.00 g, 15.33 mmol) and triethylamine (9.30 g, 92.1 mmol) was shaken *in vacuo* in a Rotaflo ampoule (*c.* 100 cm^3) in light (7 d) and the volatile material was removed *in vacuo* to give a residue which was shown by TLC to contain mainly triazadecatriene **4**. The volatile material and the residue were resealed in the ampoule *in vacuo* and heated at 115 °C (14 d). Work-up as in experiment 1 afforded unchanged triethylamine (4.98 g, 49.3 mmol, 53.5% recovered), triethylamine hydrochloride (3.59 g, 26.30 mmol, 61%) and a residue (4.65 g), which was shown by TLC (eluant: light petroleum/dichloromethane 1:2 v/v) to contain four major components (R_F 0.65, 0.30, 0.12 and 0.10) as well as base line material (tar).

The four major components were separated by DCFC (same eluant) to give (i) triazadecatriene **4** (0.82 g, 2.5 mmol, 17%), (ii) 3,10-diethyl-4,7-bis(trifluoromethyl-3,5,6,10-tetra-azadodeca-4,6,8-triene (**8**) (0.66 g, 1.83 mmol, 12%), which was identified by a comparison of its IR, ^1H, ^{13}C and ^{19}F NMR, and mass spectra with those reported [2], (iii) an orange solid which was identified as 3,12-diethyl-6,9-bis(trifluoromethyl)-3,7,8,12-tetra-azatetradeca-4,6,8,10-tetraene (**9**) (nc) (0.40 g, 1.04 mmol, 6%). Analysis: Found: C, 49.4; H, 5.9; N, 14.2%; M^+, 386. $C_{16}H_{24}N_4F_6$ requires: C, 49.7; H, 6.2; N, 14.5%; M, 386. Mass spectrum (*m/z*): 386 (88%, M^+); 314 [44, $(M-Et_2N)^+$]; 240 [17, $(M-2Et_2N)^+$]; 231 (26, $C_6H_3N_2F_6^+$); 193 (19, $C_8H_{12}N_2F_3^+$); 178 (85, $C_8H_{11}NF_3^+$); 125 (10, $C_7H_{13}N_2^+$); 72 (28, Et_2N^+); 69 (25, CF_3^+); 56 (29, $C_3H_6N^+$); 42 (47, $C_2H_4N^+$); 41 (14, $C_2H_3N^+$); 29 (100, $C_2H_5^+$); 27 (39, $C_2H_3^+$). IR ($\nu_{max.}$) (cm^{-1}): 3020 (w, vinylic C–H str.); 2980 (m, aliph. C–H str.); 1605 (s, C=C str.); 1550 (m, C=N str.); 1450 (m, CH_2 bend); 1375 (m, CH_3 bend); 1200–1110 (s, C–F str.); 1060 (m, C–N str.); 780 (m, CF_3 def.), and (iv) 2,8-bis(trifluoromethyl)-1,9-diaza-5-oxabicyclo[4.3.0^{1,6}]nona-2,8-dien-4-ol (**10**) (0.08 g, 0.28 mmol, 2%) which was identified by a comparison of its ^1H, ^{19}F and ^{13}C NMR spectra with those of an authentic sample (see next experiment).

Hydrolysis of 3,12-diethyl-6,9-bis(trifluoromethyl)-3,7,8,12-tetra-azatetradeca-4,6,8,10-tetraene (9)

A solution of the tetraene **9** (0.20 g, 0.52 mmol) in dichloromethane (10 cm^3) was poured on to the top of a DCFC sintered column (40–50 mm) filled with silica gel (*c.* 30 g) and left for 1 d before eluting with successive portions (10 cm^3) of dichloromethane. One product was obtained, which was identified as 2,8-bis(trifluoromethyl)-1,9-diaza-5-oxabicyclo[4.3.0^{1,6}]-nona-2,8-dien-4-ol (**10**) (nc) (0.12 g, 0.43 mmol, 84%). Analysis: Found: C, 35.1; H, 2.3; N, 10.1%; M^+ 276. $C_8H_6N_2O_2F_6$ requires: C, 35.0; H, 2.1; N, 10.0%; M, 276. M.p. 112–114 °C. ^1H NMR δ: 5.99 (dd, 1H, –OC*H*OH, J = 3.2 and 1.0 Hz); 5.67 (dt, 1H, O–CH–N, J = 7.4 and 0.4 Hz); 5.34 (dq, 1H, =CH, J = 3.2 and 1.7 Hz); 3.32 (ddq, 1H, CH_A in CH_AH_B; J_{AB} = 18.8 Hz; J = 7.4 and 1.8 Hz); 3.08 (br., 1H, OH); and 3.04 (ddd, 1H, CH_B in CH_AH_B; $J_{B,A}$ = 18.8 Hz; J = 1.0 and 0.4 Hz) ppm. ^{19}F NMR δ: +10.7 (s, CF_3); +10.0 (br., CF_3) ppm. ^{13}C NMR δ: 145.7 (q, =C–N, ^2J = 38.9 Hz); 131.9 (q, C=N, ^2J = 36.4 Hz); 119.9 (q, CF_3, ^1J = 273.7 Hz); 119.8 (q, CF_3, ^1J = 270.6 Hz); 113.0 (q, =CH, ^3J = 4.1 Hz); 85.9 (s, CH–O); 80.9 (s, CH–N); 37.3 (s, CH_2) ppm. Mass spectrum (*m/z*): 276 (73%, M^+); 259 [21, $(M-OH)^+$]; 257 [24, $(M-F)^+$]; 247 [4, $(M-CHO)^+$]; 231 (52, $C_7H_5N_2F_6^+$); 211 (72, $C_7H_4N_2F_5^+$); 207 [13, $(M-CF_3)^+$]; 181 (34, $C_6H_6NOF_3^+$); 180 (23, $C_6H_5NOF_3^+$); 138 (28, $C_6H_6N_2O_2^+$); 121 (32, $C_3N_2F_3^+$); 112 (89, $C_4H_4N_2O_2^+$); 95 (18, $C_2NF_3^+$); 76 (15, $C_4N_2^+$); 69 (100, CF_3^+); 42 (33, $C_2H_2O^+$); 41 (20, C_2HO^+); 29 (38, CHO^+). IR ($\nu_{max.}$) (cm^{-1}): 3380 (br., O–H str.); 3100 (w, vinylic C–H str.); 2960 (w, aliph. C–H str.); 1665 (w, C=C str.); 1620 (m, C=N str.); 1440 (m, CH_2 bend); 1220–1110 (s, C–F str. and C–O str.); 1075 (m, C–N str.); 1000 (s, N–N str.); 865 (m, =C–H out-of-plane bending); 780 (m, CF_3 def.).

Reactions of 2-chloro-8-ethyl-1,1,1-trifluoro-5-trifluoromethyl-3,4,8-triazadeca-2,4,6-triene (4)

(a) With ammonia

Aqueous ammonia (0.60 g, 12.4 mmol, 35% w/w) was added to a stirred solution of the triazadecatriene **4** (0.50 g, 1.55 mmol) in diethyl ether (*c.* 25 cm^3) contained in a round-bottomed flask (*c.* 50 cm^3) which was firmly stoppered and the mixture was then stirred further (20 h). The flask was opened, stirring was continued (5 h), water (2 cm^3) was added and then the ether layer was separated and the aqueous layer extracted with ether (2 × 25 cm^3). The combined extracts were dried ($MgSO_4$) and the solvent removed *in vacuo* to give a yellow crystalline solid (R_F 0.28; eluant n-pentane) which was identified as 2-amino-8-ethyl-1,1,1-trifluoro-5-trifluoromethyl-3,4,8-triazadeca-2,4,6-triene (**6**) (nc) (0.45 g, 1.48 mmol, 96%). Analysis: Found: C, 39.6; H, 4.6; N, 18.4; F, 37.7%. M^+, 304. $C_{10}H_{14}N_4F_6$ requires: C, 39.5; H, 4.6; N, 18.4; F, 37.5%; M, 304. M.p. 78–80 °C. Mass spectrum (*m/z*): 304 (88%, M^+); 235 [15, $(M-CF_3)^+$]; 193 (36, $C_4H_3N_2F_6^+$); 178 (32, $C_5H_5N_4F_3^+$); 177 (31, $C_5H_4N_4F_3^+$); 164 (11, $C_5H_5N_3F_3^+$); 152 (17, $C_4N_2F_4^+$); 148 (20, $C_4HN_3F_3^+$); 123 (20, $C_4H_4NF_3^+$), 117 (16, $C_4H_3N_2F_2^+$); 73 (40, $C_4H_{11}N^+$); 72 (16, $C_4H_{10}N^+$); 69 (23, CF_3^+); 58 (100, $C_3H_8N^+$); 56 (35, $C_3H_6N^+$); 43 (23, $C_2H_5N^+$); 42 (39, $C_2H_4N^+$); 29 (98, $C_2H_5^+$); 27 (59, $C_2H_3^+$/CHN^+). IR ($\nu_{max.}$) (cm^{-1}): 3330 and 3150 (m, N–H str.); 3025 (w,

vinylic C–H str.); 2975 and 2940 (w, aliph. C–H str.); 1660 (m, C=C str.); 1620 (br., N–H bend); 1560 (m, C=N str.); 1465 (m, CH_2 bend); 1380 (s, CH_3 bend); 1220–1095 (s, C–F str.); 1080 (m, C–N str.); 810 (m, vinylic =C–H out-of-plane bend); 720 (m, CF_3 def.).

(b) With 1-diethylaminocyclopentene (5)

A solution of the enamine **5** (1.27 g, 9.14 mmol) in anhydrous diethyl ether (10 cm^3) was added dropwise over a period of 30 min to a stirred solution of the triazadecatriene **4** (1.48 g, 4.58 mmol) in anhydrous diethyl ether (50 cm^3) under a nitrogen atmosphere and the stirring was continued (3 h). The resulting precipitate of the enamine hydrochloride (0.67 g, 3.84 mmol, 42%) was filtered off under a nitrogen atmosphere and the solvent removed from the filtrate under reduced pressure to give a dark red oil (1.98 g) which was shown by TLC (eluant: light petroleum/dichloromethane 3:1 v/v) to contain one major component (R_F 0.66). The material was observed to hydrolyse on silica and so it was purified by DCFC (same eluant) using alumina to afford 2-(2-diethylaminocyclopenten-1-yl)-8-ethyl-1,1,1-trifluoro-5-trifluoromethyl-3,4,8-triazadeca-2,4,6-triene (**17**) (nc) (1.44 g, 3.38 mmol, 74%). Analysis: Found: M^+, 426.2236. $C_{19}H_{28}N_4F_6$ requires: M, 426.2218. Mass spectrum (*m/z*): 426 (27%, M^+); 371 (55, $C_{15}H_{21}N_4F_6^+$); 299 (9, $C_{14}H_{13}N_3F_4^+$); 232 (24, $C_{11}H_{15}N_2F_3^+$); 218 (39, $C_{10}H_{13}N_2F_3^+/C_{11}H_{15}NF_3^+$); 217 (44, $C_{10}H_{12}N_2F_3^+/C_{11}H_{14}NF_3^+$); 195 (23, $C_8H_{14}N_2F_3^+$); 178 (19, $C_8H_{11}NF_3^+$); 163 (64, $C_6H_6N_2F_3^+$); 137 (40, $C_9H_{15}N^+$); 125 (48, $C_8H_{15}N^+$); 81 (30, $C_2F_3^+$); 72 (51, $C_4H_{10}N^+$); 69 (53, CF_3^+); 56 (74, $C_3H_7N^+$); 43 (45, $C_2H_5N^+$); 29 (100, $C_2H_5^+$); 27 (61, $C_2H_3^+$). IR ($\nu_{max.}$) (cm^{-1}): 3040 (w, vinylic C–H str.); 2980 and 2920 (m, aliph. C–H str.); 1660 and 1620 (m, C=C str.); 1610 (m, C=N str.); 1450 (m, CH_2 bend); 1380 (m, CH_3 bend); 1260 (m, =C–N str.); 1220–1110 (s, C–F str.); 740 (m, CF_3 def.).

Hydrolysis of 2-(2-diethylaminocyclopenten-1-yl)-8-ethyl-1,1,1-trifluoro-5-trifluoromethyl-3,4,8-triazadeca-2,4,6-triene (17)

A mixture of the triazadecatriene **17** (1.00 g, 2.35 mmol) and silica gel (3.0 g) in dichloromethane (35 cm^3) was poured on to the top of a DCFC sinter-column filled with silica gel (*c.* 30 g) and left (1 h). Elution of the column (eluant: light petroleum/dichloromethane 2:1 v/v) gave two products (R_F 0.43 and 0.21) and unchanged triazadecatriene **17** (0.08 g, 0.19 mmol, 8% recovered). The products were identified as (i) 2-(cyclopentanon-2-yl)-8-ethyl-3,4,8-triazadeca-2,4,6-triene (**18**) (nc) (0.60 g, 1.62 mmol, 75%). Analysis: Found: C, 48.3; H, 5.3; N, 11.6; F, 30.8%; M^+, 371. $C_{15}H_{19}N_3OF_6$ requires: C, 48.5; H, 5.1; N, 11.3; F, 30.7%; M, 371. Mass spectrum (*m/z*): 371 (15%, M^+); 302 [8, $(M-CF_3)^+$]; 299 [4, $(M-Et_2N)^+$]; 195 (42, $C_8H_{14}N_2F_3^+$); 193 (18, $C_8H_{12}N_2F_3^+$); 178 (40, $C_7H_7NOF_3^+$); 150 (17, $C_8H_{12}N_3^+$); 148 (22, $C_8H_{10}N_3^+$); 125 (100, $C_7H_{13}N_2^+$); 110 (19, $C_7H_{12}N^+/C_6H_8NO^+$); 109, (31, $C_6H_7NO^+$); 81 (32, $C_2F_3^+$); 72 (33, $C_4H_{10}N^+$); 69 (51, CF_3^+); 57 (27, $C_3H_7N^+$); 56 (53, $C_3H_6N^+$); 55 (44, $C_3H_3O^+$); 54 (27, $C_3H_2O^+$); 42 (48, $C_2H_4N^+$); 41 (35, $C_2H_3N^+$); 29 (91, $C_2H_5^+$); 27 (65, $C_2H_3^+$). IR ($\nu_{max.}$) (cm^{-1}): 3020 (w, vinylic C–H str.); 2990 (m, aliph. C–H str.); 1750 (s, C=O str.); 1620 (s, C=C and C=N str.); 1450 (m, CH_2 bend); 1375 (m, CH_3 bend); 1280 (s, =C–N str.); 1220–1080 (s, C–F str.); 740 (m, CF_3 def.) and (ii) 1-[1-(cyclopentanon-2-ylidine)-2,2,2-trifluoroethyl]-3-trifluoromethylpyrazole (**19**) (nc) (0.098 g, 0.33 mmol, 15%). Analysis: Found: C, 44.6; H, 3.0; N, 9.7%; M^+, 298. $C_{11}H_8N_2OF_6$ requires: C, 44.3; H, 2.7; N, 9.4%; M, 298. ^1H NMR δ: 7.48 (d, 1H, ring =CHN, J=2.8 Hz); 6.67 (d, 1H, ring =CHC–, J=2.8 Hz); 3.12 (tq, 2H, ring CH_2C=, J=7.5 Hz, J_{CF-CH}=3.0 Hz); 2.39 (t, 2H, ring CH_2C=O, J=7.5 Hz); 2.06 (pent., ring $CH_2CH_2CH_2$, J=7.5 Hz) ppm. ^{19}F NMR δ: +16.4 (s, 3F, CF_3C=N); +13.6 (t, 3F, CF_3C=C, J=3.0 Hz) ppm. ^{13}C NMR δ: 201.6 (s, C=O); 144.5 (q, ring C=N, ^2J=38.8 Hz); 141.8 (s, ring =C); 133.4 (s, ring =CHN); 126.3 (q, CF_3C=C, ^2J=45.1 Hz); 120.7 (q, CF_3, ^1J=268.6 Hz); 120.4 (q, CF_3, ^1J=276.7 Hz); 102.9 (s, ring =CHC–); 38.5 (s, CH_2C=O); 28.5 (s, CH_2C=C); 18.5 (s, CH_2) ppm. Mass spectrum (*m/z*): 298 (60%, M^+); 279 [24, $(M-F)^+$]; 270 [38, $(M-CO)^+$]; 242 [44, $(M-C_2H_4CO)^+$]; 229 [73, $(M-CF_3)^+$]; 201 [21, $(M-CO-CF_3)^+$]; 173 [100, $(M-C_2H_4CO-CF_3)^+$]; 149 (17, $C_6H_4OF_3^+$); 117 (15, $C_4H_3N_2F_2^+$); 69 (83, CF_3^+); 55 (49, $C_3H_3O^+$); 42 (30, $C_2H_2O^+$); 40 (14, $C_2H_2N^+$); 38 (30, $C_3H_2^+/C_2N^+$). IR ($\nu_{max.}$) (cm^{-1}): 3040 (w, vinylic C–H str.); 2980 and 2920 (aliph. C–H str.); 1715 (m, C=O str.); 1660 (m, C=C str.); 1610 (m, C=N str.); 1450 (m, CH_2 bend); 1260 (m, =C–N str.); 1220–1110 (s, C–F str.); 740 (m, CF_3 def.).

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