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UNSATURATED NITROGEN COMPOUNDS CONTAINING FLUORINE. PART 8 [1]. THE REACTION OF 2,5-DICHLORO-1,1,1,6,6,6-HEXAFLUORO-3,4-DIAZAHEXA-2,4-DIENE WITH TRIETHYLAMINE AND RELATED REACTIONS

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SUMMARY

Exposure of a mixture of the title azine **(1)** and triethylamine (1:2 molar ratio) to daylight gives as major products, triethylamine hydrochloride and the Δ^2-azetine CF_3C=CH-CH(NEt_2)-N-N=$CClCF_3$ **(3)**, together with trifluoroacetonitrile and tar; a single electron transfer (SET) mechanism is proposed involving the intermediacy of the enamine $Et_2NCH=CH_2$. In contrast the reaction of azine **(1)** with tri-n-propylamine in light affords the amine hydrochloride, the substituted azine CF_3CCl=N-N=$C(NPr^n_2)CF_3$ **(14)** and tar. Treatment of the heterocycle **(3)** with diethylamine results in replacement of Cl by NEt_2 to give the azetine **(6)** which is also formed when the azine CF_3CCl=N-N=$C(NEt_2)CF_3$ **(7)** is heated with triethylamine.

INTRODUCTION

Many of the reactions of the dichloroazine **(1)** and its di-iodo analogue **(2)** with nucleophiles such as primary and secondary amines, thiols and phenols which have been reported [2] were carried out in the presence of triethylamine to act as a basic catalyst and to remove the hydrogen halide liberated. In some cases small amounts of unidentified orange by-products were also formed and so an initial investigation of the reactions of the azines **(1)** and **(2)** with triethylamine was undertaken [3]. In both reactions the amine hydrohalide was produced together with an orange oil and tar. The oils each contained one major component and, although these components were not isolated in a pure state, spectral, (i.r. n.m.r.and mass) data indicated strongly that they had the molecular formula $C_{10}H_{12}F_6XN_3$ (X=Cl or I) [3].

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RESULTS AND DISCUSSION

In the present work the reaction of dichloroazine **(1)** with triethylamine has been repeated using a 1:2 molar ratio in vacuo in a sealed tube and found not to proceed in the dark. When the tube and contents were exposed to daylight and shaken at room temperature (5 days) the products were unchanged triethylamine (15% recovered), trifluoroacetonitrile (8%), triethylamine hydrochloride (62%), an orange oil consisting of one major and several minor components and tar. The major component of the oil was obtained pure by chromatography and identified as indeed having the molecular formula $C_{10}H_{12}F_6ClN_3$ (40% yield) by elemental analysis and mass (M^+, 325 and 323) spectrometry.

Corresponding reactions carried out in solvent ether with the tube shaken in light (7 days) or shaken and irradiated (16 hours) afforded the same viscous orange product in 41% and 43% yield, respectively.

The ^1H (presence of NEt_2 and =CH-CH-N or =CH-CH-Cl and ^{13}C (presence of $CF_3C{=}CHCHNEt_2$ and $CF_3CCl{=}N$) n.m.r. spectra indicated strongly that the product was the azetine **(3)** with the absence of a strong band in the i.r. spectrum near 1510 cm^{-1} ($\rangle C{=}\overset{+}{N}\text{-}\tilde{N}\text{-}$ str.) ruling out the alternative azomethinimine structure **(4)**. The possibility that the compound was the isomer **(5)** was rejected because the ^{13}C n.m.r. shift of the vinylic carbon in the $CF_3CX{=}N$-grouping (at 130 p.p.m.) was in the region expected for X=Cl (120 to 135 p.p.m.) and not for $X{=}NEt_2$ ($X{=}NR_2$ 140 to 154 p.p.m.) [1,4]. Furthermore, the base peak in the mass spectrum at m/z 193, corresponding to $(M\text{-}CF_3CCIN)^+$, was in agreement with structure **(3)** but not **(4)** or **(5)**.

However, in order to prove conclusively that the product had structure **(3)** it was treated with diethylamine (1:2 molar ratio) in ether to give the chlorine-free azetine derivative **(6)** (88%). Treatment of dichloroazine **(1)** with diethylamine (1:2 molar ratio) in ether gave the monoaminoazine **(7)** (75%) which, when heated at 130 °C (7 days) with triethylamine in a sealed tube in vacuo, also afforded compound **(6)** (50%) (Scheme 1); exposure to light at room temperature did not effect reaction between compound **(7)** and triethylamine during 14 days.

The only major difference in the ^{13}C n.m.r. spectra of the two azetines **(3)** and **(6)** was the expected replacement of the band at 130 p.p.m. ($CF_3\underline{C}Cl{=}N$-) in **(3)** by a lower-field band at 143.3 p.p.m. [$CF_3\underline{C}(NEt)_2{=}N$-] in **(6)**.

It is well established that triethylamine forms charge-transfer complexes with halogenomethanes, e.g. CCl_4 [5] and $CHCl_3$ [5,6]. In light such complexes decompose, i.e. (for CCl_4):

$$[CCl_4]\,[NEt_3] \longrightarrow CHCl_3 + Et_2NCH{=}CH_2 + HX \xrightarrow{NEt_3} Et_3\overset{+}{N}H\ Cl^-$$

and free halogenomethyl radicals may or may not be involved [5].

Evidence has been put forward [7] for the intermediacy of the aminoalkyl radical Et_2NCHCH_3 as a precursor to the enamine $Et_2NCH{=}CH_2$ **(8)** and of the aminium radical cation p-$MeC_6H_4NEt_2$ as a precursor to the enamine p-$MeC_6H_4NEtCH{=}CH_2$ in the photoreactions of ketones with the tertiary amines Et_3N and p-$MeC_6H_4NEt_2$, but it was not established if the aminium ions were precursors to the aminoalkyl radicals. However, in the visible light induced reduction of the ortho-quinone, β-lapachone, with triethylamine a single electron transfer (SET) mechanism was proposed via the radical cation NEt_3 leading to the radical Et_2NCHCH_3 and the immonium ion $Et_2N{=}CHMe$ and hence the enamine **(8)** [8].

From the cycloaddition reaction of trans-stilbene with the nitrile oxide $PhC{\equiv}\overset{+}{N}\text{-}\overset{-}{O}$ **(9)** (generated from PhCCl=NOH + NEt_3) a 1:1 adduct of **(9)** and the enamine **(8)**, i.e. isoxazoline **(10)**, was isolated as a by-product [9]. It was considered that enamine **(8)** was formed via decomposition of zwitterion **(11)** (Scheme 2).

For the present reaction it is proposed that a SET mechanism is involved leading to the formation of the monohydroazine **(12)**, enamine **(8)** and the salt $Et_3\overset{+}{N}H\ Cl^-$. The azine **(12)** then undergoes a base (Et_3N)–catalysed 1,4-dehydrochlorination to give two equivalents of trifluoroacetonitrile most of which was eventually converted to tar via base-catalysed telomerisation. Nucleophilic attack on dichloroazine **(1)** by enamine **(8)** afforded an intermediate zwitterion which cyclized to the azetidine **(13)** and this on dehydrochlorination by the amine gave the azetine **(3)** (Scheme 3).

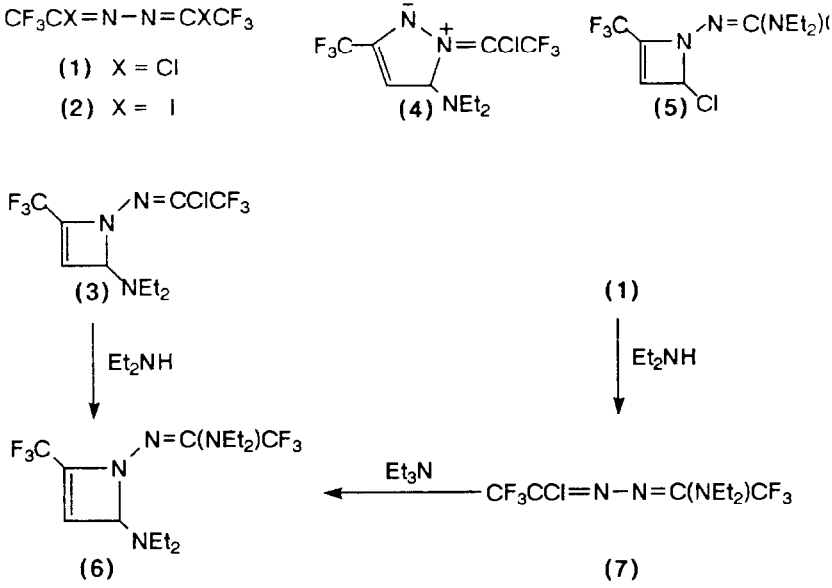
The proposed overall reaction, i.e.

$$2(1) + 4Et_3N \longrightarrow (3) + 2CF_3CN + 3\ Et_3\overset{+}{N}H\ Cl^-$$

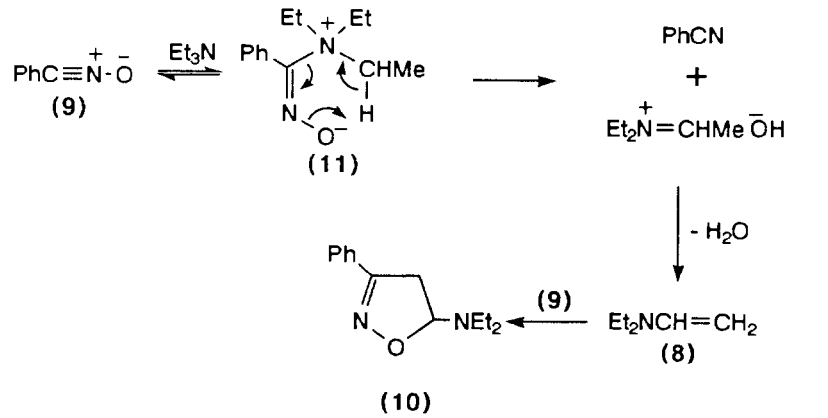
involves the formation of three equivalents of salt for each equivalent of **(3)**. In the three reactions carried out the ratio of salt $Et_3\overset{+}{N}H\ Cl^-$ to **(3)** varied between 3.11 and 3.13 and the yields of **(3)** were high (80 to 86% of theoretical).

From the preliminary investigation [3] it is apparent that the di-iodoazine **(2)** underwent a corresponding reaction with triethylamine to give the iodo analogue of compound **(3)**.

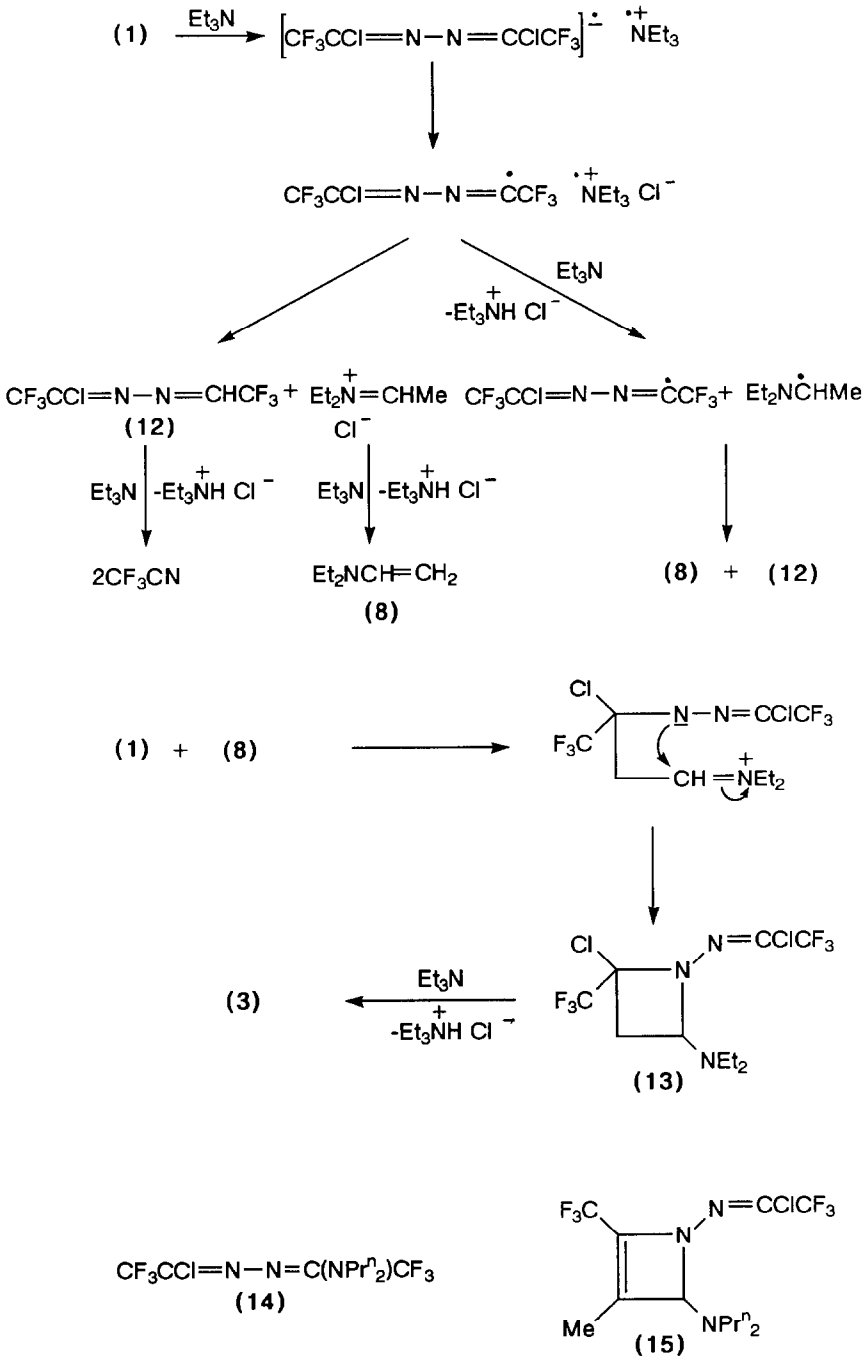
In order to determine if higher tertiary amines on treatment with dichloroazine **(1)** would also form azetines the reaction of tri-n-propylamine with



Scheme 1.



Scheme 2.


(1)
Et3N
[CF3CCl=N–N=CClCF3]
NEt3
CF3CCl=N–N=CCF3
NEt3 Cl
Et3N
-Et3NH Cl
CF3CCl=N–N=CHCF3 + Et2N=CHMe Cl
CF3CCl=N–N=CCF3 + Et2NCHMe
(12)
Et3N -Et3NH Cl
Et3N -Et3NH Cl
2CF3CN
Et2NCH=CH2
(8)
(8) + (12)
(1) + (8)
Cl
F3C
N–N=CClCF3
CH=NEt2
Cl
F3C
N
N=CClCF3
NEt2
(13)
(3)
Et3N
-Et3NH Cl
CF3CCl=N–N=C(NPr^n_2)CF3
(14)
F3C
N
N=CClCF3
Me
NPr^n_2
(15)

Scheme 3.

azine **(1)** (2:1 molar ratio) in solvent ether at room temperature in light was investigated. The products were tri-n-propylamine hydrochloride (59%) the monoaminoazine **(14)** (48%) and tar; the expected azetine **(15)** was not detected. Photochemical and thermal (at 50 °C in light) reactions gave almost identical yields of products. The mechanism of this reaction is under investigation.

The results reported in this paper have prompted an investigation of the reaction of dichloroazine **(1)** with a variety of enamines and the findings will be published in due course.

EXPERIMENTAL

Starting Materials

Dichloroazine **(1)** was synthesized from trifluoroacetic acid [2] and the amines employed were commercial samples which were distilled and their purity checked before use.

General techniques

Products were examined by TLC (eluant as in text) and the products purified or the individual components of mixtures separated by DCFC (SiO_2 Fluka 60 GF_{254}: product, 30:1 w/w). Purified products and separated components were examined by i.r. (Perkin-Elmer 783 instrument) and n.m.r. {(solutions in $CDCl_3$); ^1H [Bruker AC300 (300 MHz) spectrometer (external reference Me_4Si)], ^{19}F [Perkin-Elmer R32 (84.6 MHz) instrument (external reference CF_3CO_2H)] and ^{13}C [Bruker WP80 (20.1 MHz) or AC300 (75.0 MHz) spectrometers with broad band proton decoupling and D_2O as deuterium lock signal (external reference Me_4Si)]; chemical shifts to low field of reference designated positive} spectroscopy and mass [Kratos MS25 instrument under electron impact (e.i.) conditions] spectrometry.

Reaction of Dichloroazine (1)

(a) With triethylamine

A mixture of dichloroazine **(1)** (3.00 g, 11.49 mmol) and triethylamine (2.32 g, 22.99 mmol) was sealed in vacuo in a Rotaflo tube (ca. 50 cm^3) and kept in the dark for 14 days but reaction did not take place. The tube and contents were shaken at room temperature in light over 5 days and the volatile material (0.53 g)

was condensed *in vacuo* in a trap cooled to -196 °C. Fractional condensation of this material at *ca.* 0.2 mmHg through traps cooled to -196, -120 and -78 °C gave a -196 °C fraction identified as trifluoroacetonitrile (0.18 g, 1.87 mmol, 8%) (Found: M^+, 95. Calc. for C_2F_3N: *M*,95) and a combined -120 and -78 °C fraction identified as unchanged triethylamine (0.35 g, 3.46 mmol, 15% recovered).

The residue was washed from the tube with diethyl ether and the solid triethylamine hydrochloride (1.95 g, 14.23 mmol, 62%) was removed by filtration. The filtrate was washed with water (2 x 15 cm^3) then with dilute hydrochloric acid (2M, 2 x 20 cm^3), dried ($MgSO_4$) and the solvent removed under reduced pressure to afford an orange oil (2.23 g). This was shown by TLC (eluant: n-C_6H_{14}:CH_2Cl_2, 3:1 v/v) to contain one major component, several minor components and tar and the major component was separated by DCFC (same eluant) to give an orange oil identified as N-(2-chloro-3,3,3-trifluoro-1-aza)propenyl-4-diethylamino-2-trifluoromethyl-Δ^2-azetine **(3)** (nc) (R_F 0.53) (1.48 g, 4.58 mmol, 40%) (Found: C, 37.2; H, 3.8; N, 13.0; F, 35.5%, M^+, 325 and 323. $C_{10}H_{12}ClF_6N_3$ requires, C, 37.2; H, 3.7; N, 13.0; F, 35.3%; *M*, 323.5); $\nu_{max.}$ 2990m (vinylic C-H str.), 2945 and 2890m (aliph. C-H str.), 1620vs (C=N str.), 1200 to 1120vs (C-F str.) and 750s (CF_3 def.) cm^{-1}; δ_H 7.4 (1H, d, =CH, *J* 13 Hz, 5.0 (1H, d, N-CH-N, *J* 13 Hz), 3.3 (4 H, q, 2 x NCH_2, *J* 7.0 Hz) and 1.2 (6H, t, 2 CH_3, *J* 7.0 Hz) p.p.m.; δ_F + 9.0 (3F, s, CF_3CCl=) and +12.0 (3F, s, CF_3C=), p.p.m.; δ_C 152.9 (q, $CF_3\underline{C}$=C, ^2J 30.75), 151.6 (s,CF_3C=$\underline{C}$H-), 130.0 (q, $\underline{C}F_3\underline{C}Cl$=N, ^2J 40.1 Hz), 121.1 (q, $\underline{C}F_3C$=C, ^1J 277.4 Hz), 117.8 ($\underline{C}F_3CCl$=N, ^1J 273.9 Hz), 83.3 (s, N-CH-N), 51.2 and 42.3 (2 x s, 2 x NCH_2) and 14.15 and 11.1 (2 x s, 2 x CH_3) p.p.m.; *m/z* 326 and 324 [86.9% $(M+H)^+$], 325 and 323 (97.5, M^+), 288 [11.2, $(M-Cl)^+$], 193 [100, $(M-CF_3CClN)^+$], 178 (22.4, $C_7H_9F_3N_2^+$), 177 (31.3, $C_7H_8F_3N_2^+$), 69 (32.1, CF_3^+), and 56 (48.1, $C_3H_6N^+$).

A second reaction carried out with the same quantities of reactants in diethyl ether (10 cm^3) and the tube shaken in light (7 days) gave triethylamine hydrochloride (2.01 g, 14.69 mmol, 64%), azetine **(3)** (1.51 g, 4.69 mmol, 41%) and tar.

A third reaction using the same amounts of reactants and solvent with the tube shaken and irradiated (Hanovia 500W medium pressure lamp) during 16 hours gave triethylamine hydrochloride (2.11 g, 15.38 mmol, 67%), azetine **(3)** (1.59 g, 4.92 mmol, 43%) and tar.

(b) With diethylamine

A solution of freshly distilled diethylamine (2.79 g, 38.22 mmol) in anhydrous diethyl ether (*ca.* 5 cm^3) was added dropwise during 30 minutes to a stirred solution of azine **(1)** (5.00 g, 19.16 mmol) in ether (*ca.* 20 cm^3) contained in a flask

cooled to 0 °C (ice bath). The resulting material was stirred and warmed to room temperature and the precipitate of diethylamine hydrochloride (2.96 g, 27.41 mmol, 72%) was removed by filtration. The filtrate was washed with water (2 x 10 cm^3), dried ($MgSO_4$) and the ether removed (rotary evaporator) to give a yellow oil (4.62 g). This was shown by TLC [eluant:petroleum ether (b.p. 40 – 60 °C): $CHCl_3$, 3:1 v/v] to consist of one major component (R_F 0.63) purification of which by DCFC (same eluant) afforded 2-chloro-5-diethylamino-1,1,1,6,6,6,-hexafluoro-3,4-diaza-hexa-2,4-diene **(7)** (nc) (4.23 g, 16.20 mmol, 75%) (Found: C, 32.0; H, 3.3; N, 13.8; F, 38.0%; M^+, 299 and 297. $C_8H_{10}ClF_6N_3$ requires C, 32.2; H, 3.4; N, 14.1; F, 38.3%; M, 297.5) as two isomers in the ratio 1.15:1.0; $\nu_{max.}$ 2990 and 2945m (C-H str.) 1640m and 1620s (C=N str.), 1205 to 1150s (C-F str.) and 755 to 740s (CF_3 def.) cm^{-1}; δ_H 3.4 (2H, mult, 4 CH_2) and 1.3 (3H, mult, Me) p.p.m.; δ_F major isomer (minor isomer) + 8.0 (+8.5) (s, CF_3CCl) and + 12.5 (+18.0) (s, CF_3CNEt_2) p.p.m.; δ_C(major isomer (minor isomer) 146.1 (151.3) [q, $CF_3\underline{C}(NEt_2)$=, ^2J 31.5 (30.0) Hz] 128.8 (126.8 [q, $CF_3\underline{C}Cl$=, ^2J 40.0 (39.9) Hz)], 119.2 (118.1) [q, $\underline{C}F_3CNEt_2$), ^1J 279.2 (288.2) Hz], 118.0 (118.05) [q, $\underline{C}F_3CCl$, ^1J 273.4 (272.8)Hz] 46.29 (45.54) (s, NCH_2) and 14.10 (12.62 (s, Me) p.p.m., m/z 299 and 297 (37.5%, M^+), 262 [52.5; $(M\text{-}Cl)^+$], 227 and 225 [38.7, $(M\text{-}NEt_2)^+$], 167 [48.3 $(M\text{-}CF_3CClN)^+$], 166 (35.3, $C_6H_9F_3N_2^+$), 165 (58.7, $C_6H_8F_3N_2^+$), 124 (100, $C_4H_5F_3N^+$), 96 (24.9, $C_2HF_3N^+$), 72 (23.5, Et_2N^+) and 69 (74.4, CF_3^+).

(c) With tri-n-propylamine

A mixture of dichloroazine **(1)** (5.00 g, 19.15 mmol) tri-n-propylamine (5.48 g, 38.31 mmol) and anhydrous diethyl ether (ca. 10 cm^3) was sealed in vacuo in a Rotaflo tube (ca. 100 cm^3) and the tube and contents were shaken in light at room temperature for 7 days. Work up of the products as in experiment (a) gave tri-n-propylamine hydrochloride (4.04 g, 22.57 mmol, 59%) and a dark red oil (4.28 g) which was shown by TLC [eluant:petroleum ether (b.p. 40-60 °C): $CHCl_3$: 4:1 v/v] to contain one major component (R_F 0.67), several minor components and tar.

The major component was separated by DCFC (same eluant) and identified as 2-chloro-5-di-n-propylamino-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene **(14)** (nc) (2.98 g, 9.17 mmol, 48%) (Found: C, 36.6; H, 4.4; N, 12.6; F, 35.3%; M^+, 327 and 325. $C_{10}H_{14}ClF_6N_3$ requires C, 36.9; H, 4.3; N, 12.9; F, 35.0%; M, 325.5) as a mixture of two isomers in the ratio 1.2:1.0; $\nu_{max.}$ 2990 and 2945m (C-H str.) 1640 m and 1620s (C=N str.), 1205 to 1150s (C-F str.) and 755 to 740s (CF_3 def.) cm^{-1}; δ_H 3.25 (2 H, mult., N-CH_2) 1.60 (2 H, mult., C-CH_2) and 0.8 (3 H, mult., Me) p.p.m.; δ_F major isomer (minor isomer) + 9.4 (+9.5) (s, CF_3CCl) and +14.2 (+19.5) (s, $CF_3CNPr^n{}_2$), p.p.m. δ_C major isomer (minor isomer) 146.2 (151.6) [q,

$CF_3\underline{C}NPr^n{}_2$=, $^2\underline{J}$ 31.3 (29.6)Hz], 128.8 (126.9) [q, $CF_3\underline{C}Cl$=, $^2\underline{J}$ 40.0 (41.6) Hz], 119.1 (118.2) [q, $\underline{C}F_3CNPr^n{}_2$, $^1\underline{J}$ 279.6 (288.2) Hz] 117.9 (118.0) [q, $\underline{C}F_3CCl$, $^1\underline{J}$ 273.7 (272.7) Hz], 53.83 (53.82) (s, NCH_2), 22.10 (20.88) (s, C-$\underline{C}H_2$-C) and 11.11 (10.52 (s, Me) p.p.m.; m/z 328 and 326 [87.5%, $(\underline{M}+H)^+$], 327 and 325 (30.8, $\underline{M}^+$), 298 and 296 [97.9, $(\underline{M}-Et)^+$], 290 [56.1, $(\underline{M}-Cl)^+$], 256 and 254 (96.8, $(\underline{M}-C_5H_{11})^+$], 227 and 225 [26.9, $(\underline{M}-NPr^n{}_2)^+$], 195 (57.3, $(\underline{M}-CF_3CCIN)^+$], 179 (76.4 ($C_7H_{10}F_3N_2^+$), 153 (38.7, $C_6H_{10}F_3N^+$), 138 (54.2, $C_5H_7F_3N^+$), 70 (68.5, $C_4H_8N^+$), 69 (64.5, CF_3^+), 43 (100, $C_3H_7^+$), and 42 (40.6, $C_3H_6^+$).

A second experiment using the same amounts of reactants with the tube shaken and irradiated for 16 hours gave the amine hydrochloride (4.04 g, 22.57 mmol, 59%), azine **(14)** (2.97 g, 9.14 mmol, 48%) and tar, while a third experiment in which the tube was heated at 50 °C (16 hours) gave the amine hydrochloride (3.83 g, 21.39 mmol, 56%), azine **(14)** (2.84 g, 8.74 mmol, 46%) and tar.

Reaction of 2-Chloro-5-diethylamino-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene **(7)** with Triethylamine

A mixture of the azine **(7)** (4.00 g, 13.47 mmol), triethylamine (1.36 g, 13.47 mmol) and ether (ca. 10 cm^3) sealed in vacuo in a Rotaflo tube (ca. 100 cm^3) was shaken in daylight for 14 days but reaction did not take place. The tube and contents were then heated at 130 °C (7 days) and the resulting material was worked up as in experiment (a) to afford triethylamine hydrochloride (0.90 g, 6.57 mmol, 49%) and a dark orange oil (2.92 g) which was shown by TLC [eluant:petroleum ether (b.p. 40-60 °C):$CHCl_3$, 3:1 v/v] to contain two components which were separated by DCFC (same eluant) and identified as unchanged azine **(7)** (0.78 g, 2.62 mmol, 19.5% recovered and N-(2-diethylamino-3,3,3-trifluoro-1-aza)propenyl-4-diethylamino-2-trifluoromethyl-Δ^2-azetine **(6)** (nc) (R_F 0.52) (1.95 g, 5.42 mmol, 50%) (Found: C, 46.4; H, 6.3; N, 15.4; F, 32.0%; $\underline{M}^+$, 360. $C_{14}H_{22}F_6N_4$ requires C, 46.7; H, 6.1; N, 15.6; F, 31.7%; M, 360) as a mixture of two isomers in the ratio 11.3: 1.0; $\nu_{max.}$ 2990w (vinylic C-H str.), 2940 and 2890m (aliph. C-H str.), 1600vs (C=N str.), 1265s (C-F str.) and 740m (CF_3 def.) cm^{-1}; δ_H 7.6 (1 H, d, HC=, $\underline{J}$ 13 Hz), 5.1 (1H, d, - N-CH-N, $\underline{J}$ 13 Hz), 3.4 (4H, q, 2 x CH_2NCH_2, $\underline{J}$ 7.0 Hz), 3.3 (4H, q, 2 x CH_2NCH_2, $\underline{J}$ 7.0 Hz) and 1.2 (12H, 2 x t, 4 CH_3, $\underline{J}$ 7.0 Hz), p.p.m. δ_F major (minor) isomer + 11.7 (+ 13.2) (s, CF_3C=C) and +14.2 (+18.0) (s, CF_3C=N) p.p.m.; δ_C (for major isomer only) 149.2 (s, H$\underline{C}$=C), 148.1 (q, $CF_3\underline{C}$=C, $^2\underline{J}$ 29.5 Hz), 143.3 (q, $CF_3\underline{C}$=N, $^2\underline{J}$ 30.2 Hz), 122.0 (q, $\underline{C}F_3C$=C, $^1\underline{J}$ 276.7 Hz), 120.0 (q, $\underline{C}F_3C$=N, $^1\underline{J}$ 278.4 Hz), 83.49 (s, N-CH-N), 45.27 (s, CH_2N) and 14.13 (s, CH_3) p.p.m.; m/z 361 [27.5%, $(\underline{M}+H)^+$] 360 (49.0, $\underline{M}^+$), 195 (62.3;

$C_8H_{14}F_3N_2^+$), 193 (36.6, $C_8H_{12}F_3N_2^+$), 178 (18.7, $C_7H_9F_3N_2^+$), 167 (20.3; , $C_6H_{10}F_3N_2^+$), 165 (36.0; $C_6H_8F_3N_2^+$), 148 (26.1, $C_6H_{10}F_2N_2^+$), 125 (100, $C_7H_{13}N_2^+$), 72 (41.6, Et_2N^+) and 69 (15.2, CF_3^+).

Reaction of Azetine (3) with Diethylamine

Dropwise addition of a solution of diethylamine (0.23 g, 3.09 mmol) in diethyl ether (ca. 5 cm^3) to a stirred solution of the azetine **(3)** (0.50 g, 1.54 mmol) in ether (ca. 10 cm^3) over 20 minutes at room temperature followed by stirring for 20 hours gave a precipitate of diethylamine hydrochloride (0.18 g, 1.67 mmol, 85%). Removal of the solvent from the filtrate gave an orange oil (0.54 g) which was shown by TLC [eluant:petroleum ether (b.p. 40-60 °C);$CHCl_3$, 3:1 v/v] to consist of one major component (R_F 0.52). This was purified by DCFC (same eluant) to give the azetine **(6)** (0.49 g, 1.36 mmol, 88%).

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