Unsaturated nitrogen compounds containing fluorine. Part 13 [1]. Reaction of 2-[5,5-dimethyl-3,3-bis(trifluoromethyl)-1-pyrazolin-1-ylio]-1,1,1,3,3,3-hexafluoropropan-2-ide with compounds containing N=O or N−O bonds [2]

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Abstract

Reaction of the title azomethinimine (**1**) with nitrogen dioxide gives nitric oxide, hexafluoroacetone and 3,3-dimethyl-5,5-bis(trifluoromethyl)-1-pyrazoline (**2**) in high yield, while with the perfluoronitrosoalkanes R_FNO ($R_F = CF_3$ and $CF_2CF_2CF_3$) the products are hexafluoroacetone and the azimines **8a** and **8b**, respectively. The reactions involve initial [3+2] cycloaddition involving the N=O bonds, followed by elimination of hexafluoroacetone and nitric oxide to give **2** or of hexafluoroacetone to give **8**. From reaction of **1** with nitrosyl chloride the major products are nitric oxide, 7-chloro-8,8,8-trifluoro-2-methyl-4,4,7-tris(trifluoromethyl)-5,6-diazaocta-1,5-diene (**13**) and 5,5-dimethyl-3,3-bis(trifluoromethyl)-1-[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]pyrazolidine (**14**) formed via decomposition of the 1:1 adduct containing *C*-chloro and *N*-nitroso substituents. The oxyl $(CF_3)_2NO\cdot$ attacks azomethinimine **1** at carbon and the resulting 1:1 adduct decomposes to give hexafluoroacetone, the pyrazoline **2** and $(CF_3)_2N\cdot$ radicals which are trapped by the oxyl to afford the oxadiazapentane $(CF_3)_2NON(CF_3)_2$ (**19**). Secondary reaction then takes place involving attack of the oxygen atom of the oxadiazapentane on **1** at carbon to give hexafluoroacetone, *N,N*-bis(trifluoromethyl)amine and 3-methyl-5,5 bis(trifluoromethyl)-3-[*N,N*-bis(trifluoromethyl)methyl]-1-pyrazoline (**21**). This is confirmed by treatment of **1** with the oxadiazapentane **19**.

Introduction

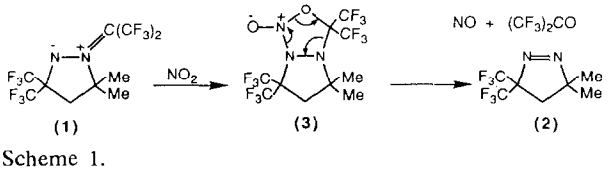
Cycloaddition [3+2] reactions of the azomethinimine **1** [3, 4] with a large variety of alkenes [1, 3, 5–8], dienes [1] and alkynes [6, 8] to afford the corresponding criss-cross adducts in high yield have been investigated, and reactions with nucleophiles [9, 10], sulphur trioxide [9], chlorine [1] and hydrogen chloride [1] have also been carried out. In a continuation of a study of the chemistry of **1**, its reactions with compounds containing the N=O bond [NO_2, R_FNO ($R_F = CF_3$ and $CF_2CF_2CF_3$) and NOCl] and the N−O bond [$(CF_3)_2NO\cdot$ and $(CF_3)_2NON(CF_3)_2$] are now reported.

Results and discussion

The reaction of azomethinimine **1** with nitrogen dioxide (*c.* 1:2 molar ratio) at room temperature (2 d) gave unchanged nitrogen dioxide (49% recovered), nitric oxide (94%), hexafluoroacetone (96%) and the 1-pyrazoline **2** (98%). These products are readily explained by initial [3+2] cycloaddition to afford adduct **3** which then underwent retrocleavage via a five-centre transition state (Scheme 1).

This represents a novel route to 1-pyrazolines containing electron-withdrawing groups which are prepared generally by the [3+2] cycloaddition of diazoalkanes to electron-deficient alkenes [11, 12]. The formation of 1-pyrazolines from the reaction of bis(trifluoromethyl)diazomethane with alkenes has not been reported, the products usually being those derived from the carbene $(CF_3)_2C:$, although the rearranged cycloadduct $(CF_3)_2CCH_2C(CN)=NNH$ has been reported from the reaction of the diazoalkane with acrylonitrile [13].

Static pyrolysis of the pyrazoline **2** at 210 °C (22 h) gave nitrogen (99%), 1,1,1-trifluoro-4-methyl-2-trifluoromethylpent-2-ene (**4**) (85%) and 1,1-dimethyl-2,2-



Scheme 1.

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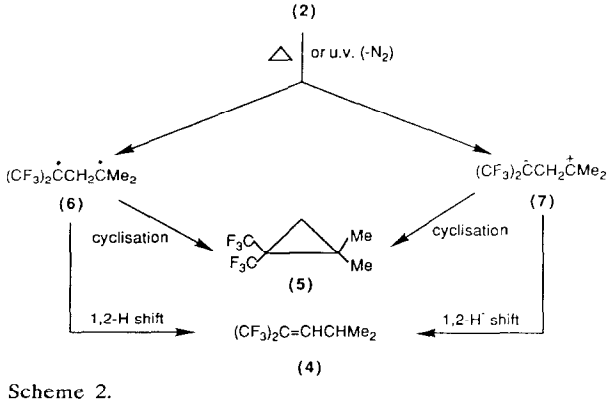
bis(trifluoromethyl)cyclopropane (**5**) (14%), while photolysis (25 h) in Pyrex gave unchanged **2** (57% recovered), nitrogen (100%), **4** (12%) and **5** (88%). In a separate experiment it was shown that cyclopropane **5** did not rearrange to alkene **4** at 210 °C.

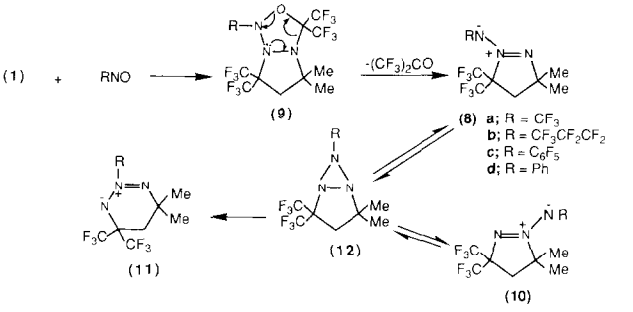
The products are consistent with the intermediacy of the 1,3-diradical **6**, formed by elimination of nitrogen from **2**, which then either cyclised or underwent a 1,2-H shift. Intermediate 1,3-diradicals have been invoked previously to explain the formation of cyclopropanes and alkenes from the thermal [14] and photochemical [15] decompositions of other 1-pyrazolines. However, 1,2-H shifts have not been proven in radical chemistry and the formation of alkene **4** is perhaps more satisfactorily explained by the intermediacy of the dipolar species **7** in which the positive charge is on a tertiary carbon and the negative charge is stabilised by the $-I$ effect of the two trifluoromethyl groups (Scheme 2).

A mixture of **1** and trifluoronitrosomethane (*c.* 1:1 molar ratio), kept at room temperature (21 d), gave hexafluoroacetone (97%) and the azimine **8a** (97%). An analogous reaction with heptafluoronitrosopropane at room temperature (6 d) gave unchanged nitrosoalkane (8% recovered), unchanged **1** (18% recovered), hexafluoroacetone (100%) and the azimine **8b** (99%). The NMR spectra of the products were consistent with the azimine structure and the IR spectra contained a strong band at *c.* 1495 cm^{-1} of comparable intensity to that at 1510 cm^{-1} (C=N−N̄ str.) in the reactant azomethinimine **1** and assigned to N=N−N̄ stretch.

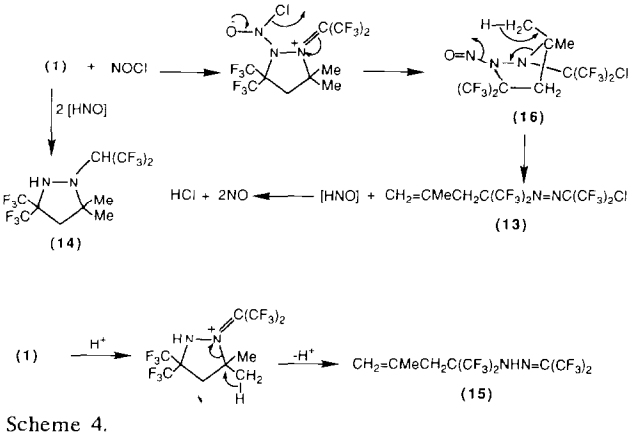
The azimines **8** are formed from the [3+2] cycloadducts **9** by retrocleavage involving elimination of hexafluoroacetone (Scheme 3). Since we reported the synthesis of the azimines **8a** and **8b** in a preliminary communication [2], Burger and coworkers have extended the scope of the reaction and prepared the corresponding azimines **8c** and **8d** from the nitroso compounds C_6F_5NO and PhNO [16]. From the ^{13}C NMR spectra obtained, they have shown conclusively that the azimines have structure **8** and were not the isomeric azimines **10** or **11**, which could be formed via rearrangement



Scheme 2.



Scheme 3.



Scheme 4.

involving the triaziridine **12**; the azimine **8c** could be isomerized photochemically to the azimine **10** (R = C_6F_5) (Scheme 3).

Azimines are relatively uncommon 1,3-dipoles and the first number of the class was synthesised in 1972; they have been reviewed [17].

The azimine **8a** was unreactive towards [3+2] cycloaddition with electron-rich alkenes ($CH_2=CH_2$ and $CH_2=CMe_2$ at 70 °C), electron-deficient alkenes [$CH_2=CHCN$ and $(NC)_2C=C(CN)_2$ at *c.* 70 °C] and nitrogen dioxide (at *c.* 20 °C). It also did not react with the nucleophiles $(MeO)_3P$ (at *c.* 20 °C) or EtOH (at 100 °C), and on static pyrolysis at 230 °C (6 h) low yields of nitrogen (12%), alkene **4** (7%) and cyclopropane **5** (3%) were formed together with an involatile black tar.

The reaction of nitrosyl chloride with **1** (*c.* 1:1 molar ratio) at room temperature (7 d) afforded nitric oxide (96%), hydrogen chloride (24%), the chlorodiazaocta-1,5-diene **13** (66%) and the pyrazolidine **14** (23%) as major products, together with unchanged **1** (2% recovered), hexafluoroacetone (2.5%), pyrazoline **2** (2.5%) and the diazaocta-1,6-diene **15** (7%). The major products and diene **15** are not consistent with [3+2] cycloaddition involving the N=O bond, but they can be explained by decomposition of the 1:1 adduct **16** as shown in Scheme 4.

Adduct **16** could have been formed from attack by the azomethinimine terminal nitrogen on the nitrosyl chloride, with elimination of chloride ion which is trapped at the carbon terminus of the 1,3-dipole. Ring-opening of **16** with elimination of the HNO molecule then gave the chlorodiene **13**. The liberated HNO reduced azomethinimine **1** to the pyrazolidine **14** with release of nitric oxide, and also reacted with nitrosyl chloride to afford hydrogen chloride and nitric oxide. The combined yields of pyrazolidine **14** and hydrogen chloride isolated require the formation of HNO (and hence chlorodiene **13**) in 70% yield and would lead to nitric oxide (94%); the isolated yields of chlorodiene **13** (66%) and nitric oxide (96%) are in excellent agreement. The hydrogen chloride formed will catalyse the rearrangement of unreacted **1** to the octa-1,6-diene **15** as has been observed previously [1].

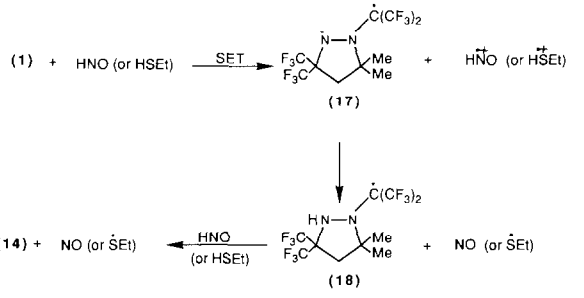
It is also possible that chlorodiene **13** and hydrogen chloride are formed to a minor extent by reaction of **1** with chlorine (present in the NOCl from the equilibrium $2NOCl \rightleftharpoons 2NO + Cl_2$), since chlorodiene **13** is a product from the treatment of **1** with chlorine [1].

The remaining minor products, hexafluoroacetone and pyrazoline **2** formed in equimolar amounts, probably arise from reaction of **1** with nitrogen dioxide impurity present in the nitrosyl chloride (prepared by the reaction $KCl + 2NO_2 \rightarrow NOCl + KNO_3$).

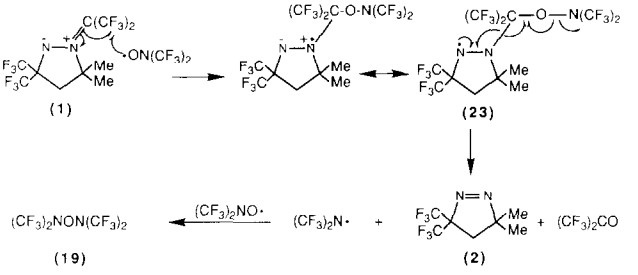
It has been reported previously [9] that **1** is reduced to pyrazolidine **14** in 33% yield by ethanethiol, but the reported melting point for **14** (44–45 °C) is much lower than that (73 °C) determined for the compound in the present work. However, the IR, ^1H and ^{19}F NMR spectral data we have obtained for **14** are in complete agreement with the data reported [9].

The mechanism of the reduction of **1** by both HNO and EtSH is of interest, and it is possible that **1** has some diradical character and can abstract hydrogen atoms from HNO and EtSH. However, an alternative, and perhaps more likely explanation is that a single electron transfer (SET) mechanism is operative to give the radical anion **17** and the radical cation $\dot{H}\overset{+}{N}O$ or $Et\dot{S}H$. Proton transfer from the radical cation to **17** would give radical **18** which is converted into pyrazolidine **14** by hydrogen-atom abstraction (Scheme 5). It is possible that proton transfer precedes SET.

The reaction of an excess of the oxyl $(CF_3)_2NO\cdot$ with **1** at room temperature (12 d) afforded hexafluoroacetone (100%), the amine $(CF_3)_2NH$ (22%), the hydroxylamine $(CF_3)_2NOH$ (6%), the oxadiazapentane **19** (*c.* 50%) contaminated with a small amount of tetrakis(trifluoromethyl) hydrazine **20**, pyrazoline **2** (71%), an unexpected product identified as the *N,N*-bis(trifluoromethyl)amino-substituted 1-pyrazoline **21** (19%) and several minor unidentified compounds. The possibility that the $(CF_3)_2N$-substituted product was the



Scheme 5.



Scheme 6.

tetrahydropyridazine **22** and not the 1-pyrazoline **21** was discounted because the MS base peak was at *m/z* 166 $[(CF_3)_2NCH_2^+]$ and the CH_2 protons absorbed at δ 3.61 and 3.25 ppm in the ^1H NMR spectrum in the region expected for a $(CF_3)_2NCH_AH_B$ grouping.

To determine whether compound **21** was formed from attack by the oxadiazapentane **19** on the 1,3-dipole **1**, the reaction of **19** with **1** (1:1 molar ratio) at room temperature (2 d) was carried out. This gave unchanged **19** (24% recovered), unchanged **1** (25% recovered), a mixture of hexafluoroacetone and the amine $(CF_3)_2NH$, hydrazine **20** (32%), pyrazoline **2** (32%) and **21** (65%).

The major products from the oxyl reaction can be explained via oxyl attack at the carbon terminus of azomethinimine **1** (attack at the nitrogen terminus would give a much weaker N–O bond) to give the radical **23**. Decomposition of **23** by β-scission afforded pyrazoline **2**, hexafluoroacetone and $(CF_3)_2N\cdot$ radicals, which were trapped by the excess of oxyl to form the oxadiazapentane **19** (Scheme 6). This formation of **19** is analogous to its normal method of preparation, i.e. ref. 18.

$$2(CF_3)_2NO\cdot + CF_3NO \longrightarrow$$
$$CF_3NO_2 + (CF_3)_2N\cdot + (CF_3)_2NO\cdot \longrightarrow$$
$$(CF_3)_2NON(CF_3)_2$$

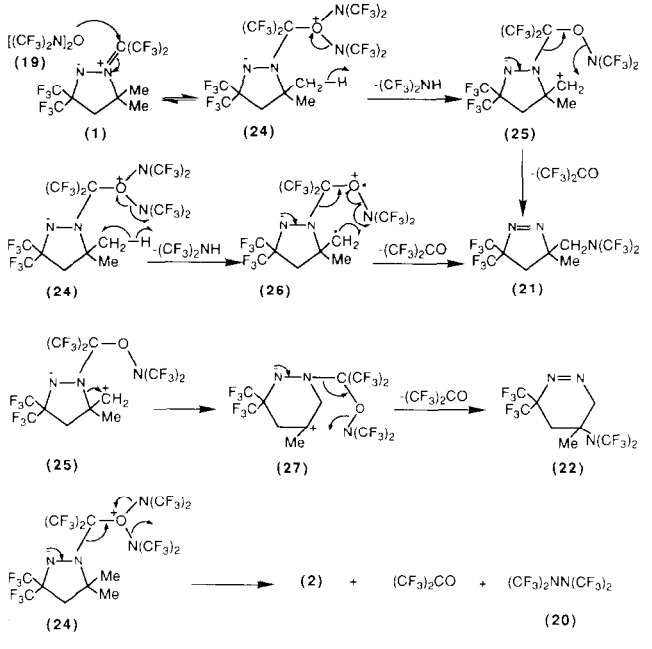
Of the remaining products, the amine $(CF_3)_2NH$, hydrazine **20** and compound **21** or **22** were formed from reaction of **19** with **1**, and the small amount of hydroxylamine $(CF_3)_2NOH$ isolated indicated that some

hydrogen abstraction by oxyl had taken place, presumably leading to the minor unidentified products.

It was also observed in a separate experiment that pyrazoline **2** did not react with the oxyl (1:2 molar ratio) under the reaction conditions.

The products derived from reaction of the oxadiazapentane **19** with **1** can be rationalised by initial attack of **19** at the carbon terminus of the 1,3-dipole **1**. The usual reaction of **19** with substrates, i.e. homolytic fission of a weak N–O bond followed by $(CF_3)_2N\cdot$ radical attack [19] clearly did not occur, since products derived from such attack at the C or N termini of **1**, were not detected. Attack on **1** presumably involved an oxygen lone pair in **19** to give the zwitterion **24** containing the $(CF_3)_2C-O$ bond, which would ultimately be eliminated as hexafluoroacetone. Elimination of the amine $(CF_3)_2NH$ from **24** could occur by an ionic or radical pathway via a seven-centre transition state, leading to the carbocation **25** or radical **26**. Transfer of the anion $(CF_3)_2N^-$ to the carbocation centre in **25**, or of the radical $(CF_3)_2N\cdot$ to the radical centre in **26**, would afford the 1-pyrazoline **21**, while rearrangement of the primary carbocation **25** to the more stable tertiary carbocation **27** by a cyclodiaza-alkide shift followed by $(CF_3)_2N^-$ transfer would give the tetrahydropyridazine **22** (Scheme 7).

The pyrazoline **2** and hydrazine **20** were isolated in approximately equimolar amounts and it is possible that they were formed by decomposition of zwitterion **24**; a feasible mechanism is shown in Scheme 7.



Scheme 7.

Experimental

Starting materials

Azomethinimine **1** was prepared (83%) by the reaction of hexafluoroacetone azine with 2-methylpropene in a sealed Rotaflo tube at room temperature [3, 4]. Nitrogen dioxide was a commercial sample and the perfluoronitrosoalkanes were research samples available in this department, the purity of each being checked (IR spectroscopy, molecular weight) before use. Nitrosyl chloride was made by the reaction of nitrogen dioxide with an excess of potassium chloride (predried at 250 °C) *in vacuo* in a sealed Rotaflo tube at room temperature [20]. The oxyl $(CF_3)_2NO\cdot$ was prepared by oxidation ($KMnO_4/H_2SO_4$) of *N,N*-bis(trifluoromethyl)hydroxylamine [21] and it was converted into the oxadiazapentane **19** by treatment with trifluoronitrosomethane *in vacuo* in a sealed Rotaflo tube [18].

General techniques

Reactions involving azomethinimine **1** were carried out *in vacuo* in sealed Rotaflo tubes (50–100 cm^3). Pyrolyses and photolysis were performed *in vacuo* in sealed Pyrex tubes (*c.* 50 cm^3).

Volatile products were separated, where necessary, by fractional condensation in a conventional vacuum system at low pressure (1–2 mmHg) through traps cooled to progressively lower temperatures. Higher-boiling mixtures were separated into their individual components by preparative-scale GLC using columns (4 or 5 m, 3–4 mm i.d.) packed with Celite impregnated (*c.* 25% w/w) with Silicone elastomer (SE30), Apiezon L grease (APL), dinonyl phthalate (DNP) or trixylyl phosphate (TXP).

Products were examined by IR spectroscopy (Perkin-Elmer 197 or 257 instruments), ^1H NMR [Perkin-Elmer R32 (90.0 MHz) or Varian Associates HA100 (100.0 MHz) spectrometers; internal reference tetramethylsilane (Me_4Si)] and ^{19}F NMR spectroscopy [Perkin-Elmer R32 (84.6 MHz) or Varian Associates HA100 (94.1 MHz) instruments; reference external trifluoroacetic acid (TFA)] and mass spectrometry (A.E.I. MS902 instrument with an electron beam energy of 70 eV). The NMR spectra were recorded using neat liquids or solutions in CCl_4 as given in the text and chemical shifts to low field of reference are designated positive.

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

Reactions of azomethinimine 1

(a) With nitrogen dioxide

A mixture of azomethinimine **1** (3.15 g, 8.20 mmol) and nitrogen dioxide (0.73 g, 15.87 mmol), shaken at room temperature (2 d), gave volatile material which was separated by fractional condensation *in vacuo* into

(i) a −196 °C fraction (0.59 g, 15.50 mmol; M, 38.1), shown (IR spectroscopy) to be a mixture of unchanged nitrogen dioxide (0.36 g, 7.83 mmol, 49% recovered) and nitric oxide (0.23 g, 7.67 mmol, 94%), and (ii) a −140 °C fraction (1.30 g, 7.83 mmol, 96%) (Analysis: Found: M, 164. Calc. for C_3F_6O: M, 166) identified (IR spectroscopy) as hexafluoroacetone.

The non-volatile material (1.96 g) was purified by low-pressure distillation (9 mmHg) to give 3,3-dimethyl-5,5-bis(trifluoromethyl-1-pyrazoline (**2**) (nc) (1.86 g, 7.95 mmol, 97%) (Analysis: Found: C, 35.9; H, 3.2; F, 48.7; N, 12.0%. $C_7H_8F_6N_2$ requires: C, 35.9; H, 3.4; F, 48.7; N, 12.0%), b.p. 128 °C/742 mmHg. IR $\nu_{max.}$ (cm^{-1}): 1574 (m) (N=N str.); 1293–1210 (s) (C−F str.); 741 (s) (CF_3 def.). ^1H NMR (neat) δ: 1.52 (s, 2H, CH_2); 1.12 (s, 6H, CMe_2) ppm. ^{19}F NMR δ: +5.9 (s, CF_3) ppm. MS *m/z*: 206 [0.3%, $(M-N_2)^+$]; 145 (35.6, $C_4H_2F_5^+$); 137 (15.5, $C_6H_8F_3^+$); 97 (17.1, $C_3H_4F_3^+$); 69 (78.1, CF_3^+); 61 (100.0, $C_3H_6F^+$); 42 (53.2, $C_3H_6^+$).

(b) With trifluoronitrosomethane

A mixture of **1** (2.76 g, 7.19 mmol) and trifluoronitrosomethane (0.73 g, 7.37 mmol), shaken at room temperature (21 d), gave volatile material which was separated by fractional condensation *in vacuo* into (i) a −196 °C fraction consisting of unchanged trifluoronitrosomethane (0.02 g, 0.20 mmol, 3% recovered) and (ii) a −140 °C fraction identified (IR spectroscopy) as hexafluoroacetone (1.16 g, 6.99 mmol, 97%).

The non-volatile product (2.30 g) was purified by sublimation *in vacuo* and identified as 2-[3,3-dimethyl-5,5-bis(trifluoromethyl)-1-pyrazolin-1-ylio]-1,1,1-trifluoro-2-azaethan-2-ide (**8a**) (nc) (2.21 g, 6.97 mmol, 97%) (Analysis: Found: C, 30.4; H, 2.6; F, 54.0; N, 13.1%; M^+, 317. $C_8H_8F_9N_3$ requires: C, 30.3; H, 2.5; F, 53.9; N, 13.2%; M, 317), m.p. 31–32 °C, b.p. 175 °C/743 mmHg. IR $\nu_{max.}$ (cm^{-1}): 1496 (s) (azimine $-\bar{N}-N=N$ str.); 1290–1210 (s) (C−F str.); 745 (s) (CF_3 def.). ^1H NMR (CCl_4) δ: 2.57 (s, 2H, CH_2); 1.55 (s, 6H, CMe_2) ppm. ^{19}F NMR δ: +11.0 (s, 3F, CF_3N); +6.2 [s, 6F, $(CF_3)_2C$] ppm. MS *m/z*: 317 (9.0%, M^+); 302 [100.0, $(M-Me)^+$]; 298 [4.2, $(M-F)^+$]; 136 (11.1, $C_6H_7F_3^+$); 69 (64.3, CF_3^+); 61 (16.2, $C_3H_6F^+$); 42 (14.6, $C_3H_6^+$).

(c) With n-heptafluoronitrosopropane

A mixture of **1** (1.79 g, 4.66 mmol) and n-heptafluoronitrosopropane (0.96 g, 4.82 mmol) shaken at room temperature (6 d), gave (i) volatile material (0.72 g, 4.23 mmol; M, 169), which was shown (IR spectroscopy) to be a mixture of hexafluoroacetone (0.64 g, 3.82 mmol, 100%) and unchanged n-heptafluoronitrosopropane (0.08 g, 0.38 mmol, 8% recovered), and (ii) a non-volatile fraction (2.04 g) which was separated by preparative-scale GLC (4 m APL at 100 °C) into its two major components, identified as unchanged **1** (0.32 g, 0.84 mmol, 18% recovered) and 2-[3,3-dimethyl-5,5-bis(trifluoromethyl)-1-pyrazolin-1-ylio]-1,1,1,2,2,3,3-heptafluoro-4-azabutan-2-ide (**8b**) (nc) (1.59 g, 3.81 mmol, 99%, 82% conversion) (Analysis: Found: C, 28.9; H, 2.1; F, 59.5; N, 10.1%; M, 417. $C_{13}H_8F_{13}N_3$ requires: C, 28.8; H, 1.9; F, 59.2; N, 10.1%; M, 417), m.p. 24–26 °C. IR $\nu_{max.}$ (cm^{-1}): 1493 (s) (azimine $-\bar{N}-N=N$ str.); 1294–1210 (s) (C−F str.); 742 (m) (CF_3 def.). ^1H NMR (neat) δ: 2.29 (s, 2H, CH_2); 1.19 (s, 6H, CMe_2) ppm. ^{19}F NMR δ: +4.6 (t, CF_3, J=7 Hz); +4.3 [s, 6F, $(CF_3)_2C$]; −31.8 (sextet, CF_2N, J=7 Hz); −53.1 (t, CF_2, J=7 Hz) ppm. MS *m/z*: 417 (1.4%, M^+); 402 [58.8, $(M-Me)^+$]; 298 [28.2, $(M-C_2F_5)^+$]; 169 (43.9, $C_3F_7^+$); 145 (28.4, $C_3F_5N^+$); 95 (30.9, $C_3H_2F_3^+$); 69 (100.0, CF_3^+); 61 (34.8, $C_3H_6F^+$); 42 (40.0, $C_3H_6^+$).

(d) With nitrosyl chloride

A mixture of **1** (2.84 g, 7.40 mmol) and nitrosyl chloride (0.45 g, 6.87 mmol), shaken at room temperature (7 d), gave volatile material (0.29 g) which was separated by fractional condensation *in vacuo* into (i) a −196 °C fraction (0.26 g, 8.21 mmol; M, 31.3), which was shown (IR spectroscopy) to be a mixture of nitric oxide (0.20 g, 6.57 mmol, 96%) and hydrogen chloride (0.06 g, 1.64 mmol, 24%), and (ii) a −140 °C fraction identified as hexafluoroacetone (0.03 g, 0.16 mmol, 2%).

The higher-boiling material (3.00 g) was separated by preparative-scale GLC (5 m SE30 at 85 °C) into its five components (A–E) (ratio 2:7:66:23:2).

Components A and E were identified as the 1-pyrazoline **2** (0.03 g, 0.13 mmol, 2%) and unchanged azomethinimine **1** (0.07 g, 0.18 mmol, 2% recovered), respectively.

Component B was identified as 8,8,8-trifluoro-2-methyl-4,4,7-tris(trifluoromethyl)-5,6-diazaocta-1,6-diene (**15**) (0.20 g, 0.52 mmol, 7%) (Analysis: Found: C, 31.2; H, 2.1; N, 7.4%; M^+, 384. Calc. for $C_{10}H_8F_{12}N_2$: C, 31.3; H, 2.1; N, 7.3%; M, 384) by a comparison of its IR, ^1H and ^{19}F NMR and mass spectra with those reported [9].

Component C was identified as 7-chloro-8,8,8-trifluoro-2-methyl-4,4,7-tris(trifluoromethyl)-5,6-diazaocta-1,5-diene (**13**) (2.03 g, 4.85 mmol, 66%) (Analysis: Found: C, 28.7; H, 1.8; N, 6.6%. Calc. for $C_{10}H_7ClF_6N_2$: C, 28.7; H, 1.7; N, 6.7%) by a comparison of its IR, ^1H and ^{19}F NMR and mass spectra with those reported [1].

Component D was identified as 5,5-dimethyl-3,3-bis(trifluoromethyl)-1-[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]pyrazolidine (**14**) (0.66 g, 1.71 mmol, 23%) (Analysis: Found: C, 31.2; H, 2.9; F, 59.5; N, 7.1%; M^+, 386. Calc. for $C_{10}H_{10}F_{12}N_2$: C, 31.1; H, 2.6; F, 59.0; N, 7.3%; M, 386), m.p. 73 °C, lit. value [9]: m.p. 44–45 °C. IR $\nu_{max.}$ (cm^{-1}): 3210 and 3120 (w) (N−H str.); 1290–1212 (s) (C−F str.); 725 (m) (CF_3 def.).

^{1}H NMR (CCl_4) δ: 4.26 (b, 1H, NH); 3.72 [sept., 1H, $(CF_3)_2CH$, $J=7$ Hz]; 2.29 (s, 2H, CH_2); 1.23 (s, 6H, CMe_2) ppm. ^{19}F NMR δ: +10.9 [d, 6F, $(CF_3)_2CH$]; +4.3 [s, 6F, $(CF_3)_2C$] ppm. MS *m/z*: 386 (12.1%, M^+); 371 [100.0, $(M-Me)^+$]; 235 (14.8, $C_5H_4F_9^+$); 95 (11.3, $C_3H_2F_3^+$); 81 (11.6, $C_2F_3^+$); 69 (20.5, CF_3^+); 57 (17.7, $C_3H_2F^+$); 56 (19.9, $C_4H_8^+$); 55 (20.1, $C_4H_7^+$); 43 (22.3, $C_3H_7^+$).

(e) With N,N-bis(trifluoromethyl)amino oxyl

A mixture of **1** (1.83 g, 4.77 mmol) and the oxyl (1.37 g, 8.16 mmol), shaken at room temperature (12 d), gave volatile material (1.74 g) which was separated by fractional condensation *in vacuo* into (i) a combined −196 °C and −140 °C fraction (1.09 g, 6.72 mmol; M, 163), which was shown by careful integration of the ^{19}F NMR spectrum to consist of hexafluoroacetone (0.79 g, 4.77 mmol, 100%), *N,N*-bis(trifluoromethyl)-amine (0.27 g, 1.77 mmol, 22%) and unchanged oxyl (0.03 g, 0.18 mmol, 2% recovered), and (ii) a −95 °C fraction (0.65 g, 2.03 mmol, 50% based on oxyl), identified as perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) (**19**) by a comparison of its IR and ^{19}F NMR spectra with those of an authentic sample prepared in the present work.

The higher-boiling material (1.45 g) was separated by preparative-scale GLC (4 m TXP at 85 °C) into its three major components (ratio 1:12:3) identified as (i) *N,N*-bis(trifluoromethyl)hydroxylamine (0.08 g, 0.45 mmol, 6%) by comparison of its IR spectrum with that of an authentic sample, (ii) 3,3-dimethyl-5,5-bis(trifluoromethyl)-1-pyrazoline (**2**) (0.80 g, 3.40 mmol, 71%) and (iii) 3-methyl-5,5-bis(trifluoromethyl)-3-[*N,N*-bis(trifluoromethyl)aminomethyl]-1-pyrazoline (**21**) (nc) (0.35 g, 0.92 mmol, 19%) (Analysis: Found: C, 27.9; H, 1.9; F, 59.7; N, 11.1%. $C_9H_7F_{12}N_3$ requires: C, 28.1; H, 1.8; F, 59.2; N, 10.9%), b.p. 165 °C/750 mmHg. IR $\nu_{max.}$ (cm^{-1}): 1577 (m) (N=N str.); 1290–1200 (s) (C−F str.); 744 (s) (CF_3 def.). ^{1}H NMR (neat) δ: 3.61 and 3.25 (AB, 2H, NCH_AH_B, $J=16$ Hz); 1.82 and 1.65 (AB, 2H, CH_AH_B, $J=18$ Hz); 1.25 (s, 3H, CH_3) ppm. ^{19}F NMR δ: +19.0 [s, 6F, $(CF_3)_2N$]; +5.3 [s, 6F, $(CF_3)_2C$] ppm. MS *m/z*: 205 (3.7%, $C_7H_7F_6^+$); 193 (46.9, $C_5H_5F_6N^+$); 166 (100.0, $C_3H_2F_6N^+$); 145 (23.1, $C_4H_2F_5^+$); 78 (36.1, $C_2H_2F_2N^+$); 69 (58.9, CF_3^+); 41 (15.1, $C_3H_5^+$).

Attempted reaction of 1-pyrazoline **2** (2.19 g, 9.4 mmol) with the oxyl (2.99 g, 17.8 mmol) *in vacuo* at room temperature (7 d) gave a quantitative recovery of the reactants.

(f) With perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) (19)

A mixture of **1** (1.71 g, 4.45 mmol), and the diazapentane **19** (1.41 g, 4.41 mmol), shaken at room temperature (2 d), gave volatile material (1.57 g) which was separated by fractional condensation *in vacuo* into (i) a combined −196 °C and −130 °C fraction (0.88 g, 5.47 mmol; M, 161), shown (IR spectroscopy) to be a mixture of hexafluoroacetone and *N,N*-bis(trifluoromethyl)amine, and (ii) a −95 °C fraction (0.68 g) identified (IR and ^{19}F NMR spectroscopy) as a mixture of unchanged diazapentane **19** (0.35 g, 1.09 mmol, 24% recovered) and tetrakis(trifluoromethyl)hydrazine (**20**) (0.33 g, 1.09 mmol, 32%) (comparison of IR spectrum with that of an authentic sample).

The non-volatile material (1.52 g) was separated into its three components (ratio 2:4:2) by preparative-scale GLC (4 m TXP at 95 °C) identified as the 1-pyrazoline **2** (0.26 g, 1.09 mmol, 32%), compound **21** (0.84 g, 2.19 mmol, 65%) and unchanged azomethinimine **1** (0.24 g, 1.09 mmol, 25% recovered).

Reactions of 3,3-dimethyl-5,5-bis(trifluoromethyl)-1-pyrazoline (2)

(a) Pyrolysis

Pyrazoline **2** (1.27 g, 5.43 mmol), heated at 210 °C (22 h), gave nitrogen (0.15 g, 5.36 mmol, 99%) (Analysis: Found: M, 28. Calc. for N_2: M, 28) and higher-boiling material (1.12 g) which was separated by preparative-scale GLC (2 m DNP at 40 °C) into its two components (ratio 85:15), 1,1,1,-trifluoro-4-methyl-2-trifluoromethylpent-2-ene (**4**) (0.95 g, 4.61 mmol, 85%), identified by a comparison of its IR, ^{1}H, ^{19}F NMR and mass spectra with those of an authentic sample [4], and 1,1-dimethyl-2,2-bis(trifluoromethyl)cyclopropane (**5**) (nc) (0.16 g, 0.78 mmol, 14%) (Analysis: Found: C, 40.6; H, 3.9; F, 55.0%; M^+, 206. $C_7H_8F_6$ requires: C, 40.8; H, 3.9; F, 55.3%; M, 206), b.p. 86 °C/750 mmHg. ^{1}H NMR (neat) δ: 1.13 (s, 6H, CMe_2); 1.05 (s, 2H, CH_2) ppm. ^{19}F NMR δ: +17.4 [s, $(CF_3)_2C$] ppm. MS *m/z*: 206 (0.8%, M^+); 159 (10.8, $C_5H_4F_5^+$); 145 (32.8, $C_4H_2F_5^+$); 137 [19.2, $(M-CF_3)^+$]; 117 (13.9, $C_6H_7F_2^+$); 97 (11.8, $C_3H_4F_3^+$); 77 (13.4, $C_3H_3F_2^+$); 69 (10.8, CF_3^+); 61 (100.0, $C_3H_6F^+$); 42 (25.5, $C_3H_6^+$); 41 (27.7, $C_3H_5^+$); 39 (21.1, $C_3H_3^+$).

(b) Photolysis

Pyrazoline **2** (2.06 g, 8.8 mmol), irradiated at a distance of 10 cm from a Hanovia S500 UV lamp (25 h), gave nitrogen (0.11 g, 3.80 mmol, 43%) (Analysis: Found: M, 28. Calc. for N_2: M, 28) and higher-boiling material (1.95 g) which was separated by preparative-scale GLC (4 m TXP at 70 °C) into its components (ratio 7:57:36) identified as the pent-2-ene **4** (0.09 g, 0.41 mmol, 11%), the cyclopropane **5** (0.69 g, 3.35 mmol, 89%) and unchanged pyrazoline **2** (1.17 g, 5.02 mmol, 57% recovered).

The cyclopropane **5** (0.206 g, 1.0 mmol), heated at 210 °C (24 h), gave unchanged cyclopropane **5** (0.196

g, 0.095 mmol, 95% recovered) and a small amount (0.01 g) of non-volatile material.

(c) With N,N-bis(trifluoromethyl)amino-oxyl

A mixture of pyrazoline **2** (2.19 g, 9.4 mmol) and the oxyl (2.99 g, 17.8 mmol), sealed *in vacuo* in a Pyrex tube (*c.* 50 cm^3) and maintained at room temperature (7 d), gave a quantitative recovery of the reactants.

Reactions of the azimine 8a

(a) Pyrolysis

The azimine **8a** (1.50 g, 4.73 mmol), heated at 230 °C (6 h), gave (i) nitrogen (0.02 g, 0.57 mmol, 12%), (ii) volatile material, which was separated by fractional condensation *in vacuo* into a −196 °C fraction (0.05 g, 0.80 mmol; M, 65), shown by GLC (2 m SE30 at 20 °C) to be a complex mixture, and a combined −95 °C and −78 °C fraction (0.10 g), shown by IR and NMR spectroscopy to consist of the pent-2-ene **4** (0.07 g, 0.33 mmol, 7%) and the cyclopropane **5** (0.03 g, 0.14 mmol, 3%), and (iii) an involatile black tar (1.22 g) which was insoluble in carbon tetrachloride.

(b) With dipolarophiles

Attempted reaction between (i) the azimine **8a** (1.29 g, 4.07 mmol), ethene (*c.* 25 mmol) and isobutene (*c.* 25 mmol) at 70 °C (24 h), (ii) the azimine **8a** (1.06 g, 3.34 mmol) and acrylonitrile (0.49 g, 9.25 mmol) at 70 °C (6 h) and (iii) the azimine **8a** (1.48 g, 4.67 mmol) and tetracyanoethene (0.60 g, 4.76 mmol) in THF (5 cm^3) at 65 °C (30 h) gave quantitative recoveries of reactants.

(c) With nucleophilic reagents

Attempted reaction between (i) the azimine **8a** (2.70 g, 8.52 mmol) and ethanol (3.50 g, 76.0 mmol) at 100 °C (21 h) and (ii) the azimine **8a** (0.89 g, 2.81 mmol) and trimethyl phosphite (0.35 g, 2.81 mmol) in THF (5 cm^3) at room temperature (24 h) gave only unchanged reactants.

(d) With nitrogen dioxide

Attempted reaction between the azimine **8a** (1.81 g, 5.71 mmol) and nitrogen dioxide (0.41 g, 8.90 mmol) at room temperature (3.5 d) gave only unchanged reactants.

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