Unsaturated nitrogen compounds containing fluorine. Part 12 [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 monosubstituted ethenes, chlorine and hydrogen chloride

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Abstract

Treatment of the title azomethinimine (**1**) with alkenes $CH_2=CHR$ ($R=CO_2H$, CHO, OCH_3, CH_2Br, CH_2Cl and OCH_2CH_2Cl) and dienes $CH_2=CRCR=CH_2$ ($R=H$ or Me) results in the regiospecific formation of the 2-substituted [3+2] cycloadducts in which the CHR group of the alkene is bonded to the nitrogen of the azomethinimine; with isoprene, major addition involves the $CH_2=CH-$ grouping. Reaction with chlorine affords a mixture of the dienes $(CF_3)_2C=NNHC(CF_3)_2CH_2CMe=CH_2$, $(CF_3)_2CClN=NC(CF_3)_2CH_2CMe=CH_2$ and $(CF_3)_2CClN=NC(CF_3)_2CH_2C(CH_2Cl)=CH_2$, while with hydrogen chloride the diene $(CF_3)_2C=NNHC(CF_3)_2CH_2CMe=CH_2$ and an adduct, possibly $(CF_3)_2CHN=NC(CF_3)_2CH_2CMe_2Cl$, are formed.

Introduction

The chemistry of the azomethinimine **1**, formed from treatment of hexafluoroacetone azine with 2-methylpropene at room temperature [2, 3], has been studied in some detail. Cycloaddition reactions of **1** with a variety of alkenes [2, 4–7] and alkynes [5, 7] have been reported and reactions with nucleophiles [8, 9], compounds containing the N–O bond [10] and sulphur dioxide [8] have also been carried out.

In the present work, further cycloadditions of **1** with monosubstituted ethenes and with buta-1,3-diene and its methyl derivatives have been investigated to determine whether or not the reactions were regiospecific. The reactions of **1** with chlorine and hydrogen chloride have also been studied.

Experimental

Starting materials

The azomethinimine **1**, m.p. 73–74 °C, was prepared (83%) by the reaction of hexafluoroacetone azine with 2-methylpropene (1:1 molar ratio) *in vacuo* in a Rotaflo tube which was shaken at room temperature (3 d) [2, 3]. All of the alkenes and dienes used were commercial samples and the purity of each was checked (IR, ^1H NMR spectroscopy, GLC) before use.

General techniques

Reactions involving the azomethinimine **1** were carried out *in vacuo* in Rotaflo tubes (25–100 cm^3).

Volatile products were separated by fractional condensation in a vacuum system, with the vapour passed at low pressure (1–2 mmHg) through traps cooled to progressively lower temperatures. Higher-boiling mixtures were separated into their components by preparative-scale GLC (Pye 104 instrument) using columns (4 m, 3–4 mm i.d.) packed with Celite impregnated (25% w/w) with Silicone elastomer (SE30) or trixylyl phosphate (TXP) at temperatures stated in the text.

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 HA 100 (94.1 MHz) instruments; reference external trifluoroacetic acid (TFA)] and mass spectrometry (A.E.I. MS 902 instrument with an electron beam energy of 70 eV). The NMR spectra were recorded using neat liquids or solutions (in CCl_4, $CDCl_3$ or acetone-d_6) as stated in the text and chemical shifts to low field of reference are designated positive.

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

Reactions of the azomethinimine 1

(a) With acrylic acid

A mixture of **1** (1.40 g, 3.65 mmol), acrylic acid (0.26 g, 3.61 mmol) and THF (3.2 g), heated at 70 °C (7 d) gave THF (3.2 g) and a white residue (1.65 g) which was recrystallised from $CHCl_3$ to afford 6,6-dimethyl-4,4,8,8-tetrakis(trifluoromethyl)-1,5-diazabicyclo[3.3.0]-octan-2-oic acid (**2a**) (nc) (1.51 g, 3.31 mmol, 92%) (Analysis: Found: C, 34.2; H, 2.8; F, 50.1; N, 6.2%; M^+, 456. $C_{13}H_{12}F_{12}N_2O_2$ requires: C, 34.2; H, 2.6; F, 50.0; N, 6.1%; M, 456), m.p. 170–172 °C. IR $\nu_{max.}$ (cm^{-1}): 3270–3050 (m) (O–H str.); 1835 (s) (C=O str.); 1320–1230 (s) (C–F str.); 762 (s) and 746 (m) (CF_3 def.). ^1H NMR ($CDCl_3$) δ: 10.8 (b, 1H, CO_2H); 4.40 (b, 1H, CHC=O); 2.99 (d, 2H, CH_2, $J=9$ Hz); 2.48 (s, 2H, CH_2); 1.36 (s, 6H, CMe_2) ppm. ^{19}F NMR δ: +10.9, +10.2, +6.4 and +5.1 (4q, $4CF_3$, $J=c.$ 10 Hz) ppm. MS *m/z*: 456 (51.0%, M^+); 442 [26.3, $(M-CH_2)^+$]; 411 [100.0, $(M-CO_2H)^+$]; 387 [26.1, $(M-CF_3)^+$]; 277 (42.5, $C_7H_9F_6O_2^+$); 247 (32.3, $C_8H_9F_6N_2^+$); 207 (46.7, $C_7H_9F_6^+$); 145 (53.1, $C_4H_2F_5^+$); 137 (43.7, $C_6H_8F_3^+$); 95 (47.9, $C_3H_2F_3^+$); 69 (71.3, CF_3^+); 61 (32.6, $C_3H_6F^+$); 56 (33.9, $C_4H_8^+$); 44 (37.6, CO_2^+); 42 (80.1, $C_3H_6^+$).

(b) With acrolein

A mixture of **1** (0.39 g, 1.02 mmol), acrolein (0.23 g, 4.11 mmol) and THF (3.3 g), shaken at room temperature (24 h), gave unchanged acrolein (0.17 g, 3.04 mmol, 74% recovered), THF (3.3 g) and a residue (0.45 g) which was extracted from the tube with CCl_4. The solvent was removed *in vacuo* and the resulting material was sublimed at reduced pressure to give a crystalline solid identified as 6,6-dimethyl-4,4,8,8-tetrakis(trifluoromethyl)-1,5-diazabicyclo[3.3.0]octan-2-al (**2b**) (nc) (0.44 g, 1.00 mmol, 98%) (Analysis: Found: C, 35.8; H, 3.0; F, 51.4; N, 6.5%; M^+, 440. $C_{13}H_{12}F_{12}N_2O$ requires: C, 35.5; H, 2.7; F, 51.8; N, 6.4%; M, 440), m.p. 63 °C. IR $\nu_{max.}$ (cm^{-1}): 1743 (s) (C=O str.); 1320–1210 (s) (C–F str.); 750 (m) (CF_3 def.). ^1H NMR (CCl_4) δ: 9.38 (b, 1H, CHO); 3.80 (t, 1H, CH–C=O, $J=9$Hz); 2.86 (d, 2H, CH_2, $J=9$ Hz); 2.63 and 2.51 (AB, 2H, CH_AH_B, $J=14$ Hz); 1.50 and 1.42 (2s, 6H, Me_2C) ppm. ^{19}F NMR δ: +11.0, +10.1, +6.3 and +5.8 (4q, $4CF_3$, $J=c.$ 10 Hz) ppm. MS *m/z*: 440 (14.0%, M^+); 411 [100.0, $(M-CHO)^+$]; 247 (18.5, $C_8H_9F_6N_2^+$); 207 (16.8, $C_7H_9F_6^+$); 145 (18.4, $C_4H_2F_5^+$); 69 (21.7, CF_3^+); 56 (16.4, $C_3H_4O^+$); 42 (28.9, $C_3H_6^+$); 41 (24.9, $C_3H_5^+$).

(c) With methyl vinyl ether

A mixture of **1** (1.16 g, 3.02 mmol), methyl vinyl ether (0.64 g, 11.03 mmol) and THF (4.0 g), shaken at room temperature (2 d), gave unchanged methyl vinyl ether (0.47 g, 8.18 mmol, 74% recovered) and THF (4.0 g), and a non-volatile residue which was identified as 2-methoxy-6,6-dimethyl-4,4,8,8-tetrakis-(trifluoromethyl)-1,5-diazabicyclo[3.3.0]octane (**2c**) (nc) (1.25 g, 2.83 mmol, 94%) (Analysis: Found: C, 35.3; H, 2.9; F, 51.8; N, 6.4%; M^+, 442. $C_{13}H_{14}F_{12}N_2O$ requires: C, 35.3; H, 3.2; F, 51.6; N, 6.3%; M, 442), m.p. 35–36 °C. IR $\nu_{max.}$ (cm^{-1}): 1320–1210(s) (C–F str.); 1150 (s, C–O str.); 750 (m) (CF_3 def.). ^1H NMR (CCl_4) δ: 4.71 (t, 1H, >CH–O, $J=6$ Hz); 3.23 (s, 3H, OMe); 2.67 (mult., 2H, CH_2–C–O); 2.48 and 2.35 (AB, 2H, CH_AH_B, $J=14$ Hz); 1.39 and 1.30 (2s, 6H, CMe_2) ppm. ^{19}F NMR δ: +11.0, +10.1, +6.5 and +5.8 (4q, $4CF_3$, $J=c.$ 10 Hz) ppm. MS *m/z*: 442 (30.9%, M^+); 411 [100.0, $(M-MeO)^+$]; 237 (25.4, $C_7H_{11}F_6N_2^+$); 235 (95.0, $C_7H_9F_6N_2^+$); 207 (28.1, $C_7H_9F_6^+$); 145 (69.6, $C_4H_2F_5^+$); 95 (40.0, $C_3H_2F_3^+$); 69 (56.7, CF_3^+); 56 (41.0, $C_4H_8^+$); 55 (29.1, $C_4H_7^+$); 42 (40.7, $C_3H_6^+$).

(d) With 2-chloroethyl vinyl ether

A mixture of **1** (0.85 g, 2.21 mmol) and the vinyl ether (2.79 g, 26.20 mmol), shaken at room temperature (18 h), gave a volatile material identified as unchanged vinyl ether (2.55 g, 23.94 mmol, 91% recovered) and a residue of 2-(2-chloroethoxy)-6,6-dimethyl-4,4,8,8-tetrakis(trifluoromethyl)-1,5-diazabicyclo[3.3.0]octane (**2d**) (nc) (1.08 g, 2.20 mmol, 100%) (Analysis: Found: C, 34.1; H, 3.3; N, 5.8%; M^+, 490/492. $C_{13}H_{15}ClF_{12}N_2O$ requires: C, 34.3; H, 3.1; N, 5.7%; M, 490.5), m.p. 32–34 °C. IR $\nu_{max.}$ (cm^{-1}) 1285–1195(s) (C–F str.); 1155 and 1095 (C–O str.); 750 (m) (CF_3 def.). ^1H NMR δ: 4.85 (t, 1H, >CH–O, $J=6$ Hz); 3.9–3.4 (mult., 4H, CH_2O and CH_2Cl); 2.90 and 2.71 (ABd, 2H, CH_AH_B, $J=14$ and 6 Hz); 2.52 and 2.39 (AB, 2H, CH_AH_B, $J=14$ Hz); 1.43 and 1.33 (2s, 6H, CMe_2) ppm. ^{19}F NMR δ: +11.0, +10.0, +6.5 and +6.0 (4q, $4CF_3$, $J=c.$ 10 Hz) ppm. MS *m/z*: 490 and 492 (12.2%, M^+); 411 [52.2, $(M-OCH_2CH_2Cl)^+$]; 341 (44.7, $C_{11}H_{10}F_9N_2^+$); 235 (58.8, $C_7H_9F_6N_2^+$); 145 (48.0, $C_4H_2F_5^+$); 95 (30.7, $C_3H_2F_3^+$); 69 (60.4, CF_3^+); 63 and 65 (100.0, $C_2H_4Cl^+$); 56 (31.9, $C_4H_8^+$); 55 (33.5, $C_4H_7^+$); 44 (48.2, C_2HF^+); 42 (57.4, $C_3H_6^+$); 41 (48.3, $C_3H_5^+$).

(e) With allyl bromide

A mixture of **1** (1.18 g, 3.07 mmol) and allyl bromide (3.62 g, 29.91 mmol), shaken at room temperature (2 h), gave unchanged allyl bromide (3.22 g, 26.61 mmol, 89% recovered) and higher-boiling material (1.58 g) which was sublimed *in vacuo* to afford 2-bromoethyl-6,6-dimethyl-4,4,8,8-tetrakis(trifluoromethyl)-1,5-diazabicyclo[3.3.0]octane (**2e**) (nc) (1.50 g, 2.97 mmol, 97%)

(Analysis: Found: C, 31.2; H, 2.7; F, 44.8; N, 5.4%; M^+, 504/506. $C_{13}H_{13}BrF_{12}N_2$ requires: C, 30.9; H, 2.6; F, 45.2; N, 5.6%; M, 505), m.p. 22–24 °C. IR $\nu_{max.}$ (cm^{-1}): 1280–1210(s) (C–F str.); 748 (m) (CF_3 def.). ^1H NMR (CCl_4) δ: 3.61 (d, 2H, CH_2Br, $J=10$ Hz); 3.15 (t, 1H, >CH–, $J=10$ Hz); 2.89 and 2.67 (AB, 2H, CH_AH_B, $J=14$ Hz); 2.55 and 2.37 (AB, 2H, CH_AH_B, $J=13$ Hz); 1.35 (s, 6H, CMe_2) ppm. ^{19}F NMR δ: +10.9, +9.9, +6.9 and +5.3 (4q, $4CF_3$, $J=c.$ 10 Hz) ppm. MS *m/z*: 504 and 506 (16.8%, M^+); 425 [30.7, $(M-Br)^+$]; 235 (51.8, $C_7H_9F_6N_2^+$); 145 (48.3, $C_4H_2F_5^+$); 95 (100.0, $C_3H_2F_3^+$); 69 (88.8, CF_3^+); 58 (40.5, $C_3H_3F^+$); 55 (50.1, $C_4H_7^+$); 43 (84.3, $C_3H_7^+$); 41 (67.5, $C_3H_5^+$); 40 (39.9, $C_3H_4^+$).

(f) With allyl chloride

A mixture of **1** (0.80 g, 2.08 mmol) and allyl chloride (2.0 g, 26.1 mmol), heated at 80 °C (1 h), gave unchanged allyl chloride (1.84 g, 24.0 mmol, 92% recovered) and a solid residue (0.94 g) which was sublimed *in vacuo* to afford 2-chloromethyl-6,6-dimethyl-4,4,8,8-tetrakis-(trifluoromethyl)-1,5-diazabicyclo[3.3.0]octane (**2f**) (nc) (0.86 g, 1.87 mmol, 90%) (Analysis: Found: C, 34.2; H, 3.0; F, 49.4; N, 6.0%; M^+, 460/462. $C_{13}H_{13}ClF_{12}N_2$ requires: C, 33.9; H, 2.8; F, 49.5; N, 6.1%; M, 460.5), m.p. 42–44 °C. IR $\nu_{max.}$ (cm^{-1}): 1300–1210 (s) (C–F str.); 765 and 745 (m) (CF_3 def.). ^1H NMR ($CDCl_3$) δ: 3.90–3.05 (AB mult., 3H, >CH– and CH_AH_BCl); 2.90–2.60 (mult., 2H, CH_2); 2.54 and 2.38 (AB, 2H, CH_AH_B, $J=13$ Hz); 1.33 (b, 6H, CMe_2) ppm. ^{19}F NMR δ: +10.2, +9.2, +7.0 and +5.6 (4q, $4CF_3$, $J=c.$ 10 Hz) ppm. MS *m/z*: 460 and 462 (7.6%, M^+); 445 and 447 [5.4, $(M-Me)^+$]; 411 [10.0, $(M-CH_2Cl)^+$]; 385 (37.1, $C_{10}H_9F_{12}N_2^+$); 301 (60.8, $C_8H_6F_9N_2^+$); 281 (39.6, $C_8H_5F_8N_2^+$); 69 (58.3, CF_3^+); 61 (100.0, $C_3H_6F^+$); 56 (98.7, $C_4H_8^+$); 55 (98.1, $C_4H_7^+$); 42 (29.2, $C_3H_6^+$); 41 (36.6, $C_3H_5^+$).

(g) With acrylonitrile

A mixture of the azomethinimine **1** (3.56 g, 9.27 mmol) and acrylonitrile (1.33 g, 25.09 mmol), shaken at room temperature (2 d), gave unchanged acrylonitrile (0.88 g, 16.60 mmol, 66% recovered) and a residue (4.01 g) which was washed from the tube with chloroform and the solvent removed *in vacuo* to afford a crystalline solid identified as 2-cyano-6,6-dimethyl-4,4,8,8-tetrakis(trifluoromethyl)-1,5-diazabicyclo[3.3.0]octane (**2i**) (4.01 g, 9.18 mmol, 99%) (Analysis: Found: C, 35.8; H, 2.6; F, 52.0; N, 9.3%; M^+, 437. Calc. for $C_{13}H_{11}F_{12}N_3$: C, 35.7; H, 2.5; F, 52.1; N, 9.6%; M, 437), m.p. 103–104 °C, (lit. value [5] m.p. 104–105 °C). IR $\nu_{max.}$ (cm^{-1}): 2268 (w) (C≡N str.); 1310–1205 (s) (C–F str.); 760 and 745 (m) (CF_3 def.) ^1H NMR (acetone-d_6) δ: 4.37 (t, 1H, CHCN, $J=8$ Hz); 3.46 and 3.12 (ABd, 2H, CH_AH_B, $J=14$ and 8 Hz); 2.69 (s, 2H, CH_2); 1.39 (s, 6H, CMe_2) ppm. ^{19}F NMR δ: +10.4 (q, 3F, CF_3, $J=10.5$ Hz); +9.0 (q, 3F, CF_3, $J=10.2$ Hz); +6.1 (q, 3F, CF_3, $J=10.2$ Hz); +5.1 (q, 3F, CF_3, $J=10.5$ Hz) ppm. MS *m/z*: 437 (78.6%, M^+); 422 [78.4, $(M-Me)^+$]; 368 [37.7, $(M-CF_3)^+$]; 258 (89.4, $C_8H_9F_6N_3^+$); 232 (100.0, $C_6H_3F_6N_3^+$); 206 (45.9, $C_7H_8F_6^+$); 186 (28.3, $C_7H_7F_5^+$); 145 (37.7, $C_4H_2F_5^+$); 137 (46.5, $C_6H_8F_3^+$); 95 (27.9, $C_3H_2F_3^+$); 69 (36.9, CF_3^+); 61 (42.7, $C_3H_6F^+$); 56 (28.7, $C_4H_8^+$); 55 (25.8, $C_4H_7^+$); 42 (29.0, $C_3H_6^+$); 41 (33.0, $C_3H_5^+$).

The adduct **2i** (1.69 g, 3.87 mmol) on static pyrolysis *in vacuo* in a sealed Pyrex tube (*c.* 100 cm^3) at 200 °C (20 h), gave 1,1-bis(trifluoromethyl)ethene (1.05 g, 6.40 mmol, 83%) (Analysis: Found: M, 165. Calc. for $C_4H_2F_6$: M, 164), a small amount of higher-boiling material (0.07 g) and an involatile tar (0.50 g).

(h) With buta-1,3-diene

A mixture of **1** (0.61 g, 1.59 mmol) and buta-1,3-diene (0.80 g, 14.8 mmol), heated at 65 °C (5 h), gave a volatile material identified as unchanged diene (0.71 g, 13.2 mmol, 89% recovered) and a residue (0.70 g) which was sublimed *in vacuo* to afford 6,6-dimethyl-4,4,8,8-tetrakis(trifluoromethyl)-2-vinyl-1,5-diazabicyclo[3.3.0]octane (**3a**) (nc) (0.64 g, 1.46 mmol, 92%) (Analysis: Found: C, 38.4; H, 3.2; N, 6.6%; M^+, 438. $C_{14}H_{14}F_{12}N_2$ requires: C, 38.4; H, 3.2; N, 6.4%; M, 438), m.p. 54–56 °C. IR $\nu_{max.}$ (cm^{-1}): 1650 (w) (C=C str.); 1300–1210 (s) (C–F str.); 700 (s) (CF_3 def.). ^1H NMR ($CDCl_3$) δ: 5.7–5.3 (mult., 1H, =CH); 5.3–5.0 (mult., 2H, $=CH_2$); 3.84 (mult., 1H, >CH–); 2.7–2.2 (mult., 4H, $2CH_2$); 1.30 (s, 6H, CMe_2) ppm. ^{19}F NMR δ: +10.1 [mult., 6F, $C(CF_3)_2$]; +6.6 and +4.4 (2q, $2CF_3$, $J=c.$ 10 Hz) ppm. MS *m/z*: 438 (32.1%, M^+); 301 (22.4, $C_8H_6F_9N_2^+$); 273 (33.4, $C_{10}H_{11}F_6N_2^+$); 235 (30.3, $C_7H_9F_6N_2^+$); 233 (40.5, $C_7H_7F_6N_2^+$); 69 (45.1, CF_3^+); 61 (100.0, $C_3H_6F^+$); 56 (56.5, $C_4H_8^+$); 55 (60.6, $C_4H_7^+$); 42 (32.4, $C_3H_6^+$); 41 (32.8, $C_3H_5^+$).

(i) With 2,3-dimethylbuta-1,3-diene

A mixture of **1** (0.72 g, 1.88 mmol), 2,3-dimethylbuta-1,3-diene (0.25 g, 3.10 mmol) and THF (3.0 g), heated at 70 °C (2 d), gave volatile material (3.14 g), shown by GLC (2 m SE30 at 40 °C) to consist of THF (3.0 g) and unchanged diene (0.11 g, 1.34 mmol, 43% recovered) and a non-volatile residue (0.83 g) which was sublimed *in vacuo* to afford 2-(1-methylvinyl)-2,6,6-trimethyl-4,4,8,8-tetrakis(trifluoromethyl)-1,5-diazabicyclo[3.3.0]octane (**3b**) (nc) (0.79 g, 1.70 mmol, 90%) (Analysis: Found: C, 41.5; H, 4.2; F, 49.0; N, 6.1%; M^+, 466. $C_{16}H_{18}F_{12}N_2$ requires: C, 41.2; H, 3.9; F, 48.9; N, 6.0%; M, 466), m.p. 73 °C. IR $\nu_{max.}$ (cm^{-1}): 1640 (w) (C=C str.); 1280–1200 (s) (C–F str.); 700 (s) (CF_3 def.). ^1H NMR (CCl_4) δ: 5.07 and 4.90 (2s, 2H, $=CH_2$); 2.99 and 2.57 (AB, 2H, CH_AH_B, $J=14$ Hz); 2.43 and

2.34 (AB, 2H, CH_AH_B, $J=14$ Hz); 1.76 (s, 3H, =CMe); 1.57 (s, 3H, Me); 1.48 and 1.29 (2s, 6H, CMe_2) ppm. ^{19}F NMR δ: +13.4 and +12.4 (2q, $2CF_3$, $J=c.$ 11 Hz); +7.9 (mult., $2CF_3$) ppm. MS *m/z*: 466 (18.8%, M^+); 261 (99.1, $C_7H_6F_9^+$); 235 (67.9, $C_7H_9F_6N_2^+$); 163 (23.7, $C_4HF_6^+$); 82 (48.7, $C_6H_{10}^+$); 69 (53.0, CF_3^+); 61 (44.5, $C_3H_6F^+$); 56 (38.5, $C_4H_8^+$); 55 (92.7, $C_4H_7^+$); 53 (76.1, $C_4H_5^+$); 42 (89.5, $C_3H_6^+$); 40 (100.0, $C_3H_4^+$); 39 (76.2, $C_3H_3^+$).

(j) With 2-methylbuta-1,3-diene

A mixture of **1** (0.78 g, 2.03 mmol) and 2-methylbuta-1,3-diene (1.62 g, 23.82 mmol) heated at 70 °C (2 h), gave volatile material, identified as unchanged diene (1.48 g, 21.77 mmol, 91% recovered), and a non-volatile residue (0.90 g) which was separated by preparative-scale GLC (4 m TXP at 130 °C) into two components (i, ii) (ratio 65:35).

(i) 6,6-Dimethyl-2-(1-methylvinyl)-4,4,8,8-tetrakis(trifluoromethyl)-1,5-diazabicyclo[3.3.0]octane (**3c**) (nc) (0.56 g, 1.28 mmol, 64%) (Analysis: Found: C, 40.1; H, 3.7; F, 50.5; N, 6.1%; M^+ 452. $C_{15}H_{16}F_{12}N_2$ requires: C, 39.8; H, 3.5; F, 50.4; N, 6.2%; M, 452), m.p. 42 °C. IR $\nu_{max.}$ (cm^{-1}): 1650 (w) (C=C str.); 1305–1210(s) (C–F str.); 705 (s) (CF_3 def.). ^1H NMR (CCl_4) δ: 4.95 and 4.83 (2s, 2H, $=CH_2$); 3.88 (t, 1H, $>CH-$, $J=8$ Hz); 2.7–2.3 (mult., 4H, $2CH_2$); 1.67 (s, 3H, =CMe); 1.37 and 1.30 (2s, 6H, CMe_2) ppm. ^{19}F NMR δ: +10.1 (mult., 6F, $2CF_3$); +6.2 and +4.1 (2q, 6F, $2CF_3$, $J=c.$ 10 Hz) ppm. MS *m/z*: 452 (27.1%, M^+); 287 (22.5, $C_{11}H_{13}F_6N_2^+$); 247 (33.3, $C_8H_9F_6N_2^+$); 235 (36.1, $C_7H_9F_6N_2^+$); 77 (16.9, $C_3H_3F_2^+$); 69 (54.1, CF_3^+); 68 (24.0, $C_5H_8^+$); 67 (32.6, $C_5H_7^+$); 61 (100.0, $C_3H_6F^+$); 56 (24.7, $C_4H_8^+$); 55 (36.4, $C_4H_7^+$); 42 (62.4, $C_3H_6^+$); 41 (35.2, $C_3H_5^+$).

(ii) 2,6,6-Trimethyl-4,4,8,8-tetrakis(trifluoromethyl)-2-vinyl-1,5-diazabicyclo[3.3.0]octane (**3d**) (nc) (0.32 g, 0.71 mmol, 36%) (Analysis: Found: C, 39.7; H, 3.8; F, 50.3; N, 5.9%; M^+ 452. $C_{15}H_{16}F_{12}N_2$ requires: C, 39.8; H, 3.5; F, 50.4; N, 6.2%; M, 452); m.p. 43–44 °C. IR $\nu_{max.}$ (cm^{-1}): 1635 (w) (C=C str.); 1288–1210 (s) (C–F str.); 702 (s) (CF_3 def.). ^1H NMR (CCl_4) δ: 6.2 (mult., 1H, =CH); 5.1–4.9 (mult., 2H, $=CH_2$); 2.62 and 2.57 (2s, 4H, $2CH_2$); 1.46 (s, 3H, Me); 1.37 (s, 6H, CMe_2) ppm. ^{19}F NMR δ: +10.9 and +10.2 (2q, $2CF_3$, $J=c.$ 10 Hz); +8.9 (mult., $2CF_3$) ppm. MS *m/z*: 452 (35.5%, M^+); 247 (96.2, $C_8H_9F_6N_2^+$); 235 (100.0, $C_7H_9F_6N_2^+$); 149 (78.9, $C_4H_6F_5^+$); 135 (32.9, $C_3H_4F_5^+$); 108 (99.9, $C_4H_3F_3^+$); 69 (64.2, CF_3^+); 57 (67.4, $C_3H_2F^+$); 56 (34.8, $C_4H_8^+$); 55 (60.0, $C_4H_7^+$); 44 (55.7, C_2HF^+); 43 (50.3, $C_3H_7^+$); 41 (70.7, $C_3H_5^+$).

(k) With chlorine

A mixture of **1** (2.58 g, 6.72 mmol) and chlorine (0.50 g, 7.04 mmol), shaken at room temperature (4 d), gave volatile material, which was identified as hydrogen chloride (0.16 g, 4.28 mmol, 61%), and higher-boiling material (0.92 g) which was extracted with carbon tetrachloride to give soluble material (1.43 g) and a residue (1.47 g). The soluble fraction was separated by preparative-scale GLC (4 m SE30 at 110 °C) into three components (A–C) (ratio 12:11:26).

Component A was identified as 8,8,8-trifluoro-2-methyl-4,4,7-tris(trifluoromethyl)-5,6-diazaocta-1,6-diene (**5**) (0.32 g, 0.82 mmol, 12%) (Analysis: Found: C, 31.5; H, 2.2; F, 58.9; N, 7.6%; M^+, 384. Calc. for $C_{10}H_8F_{12}N_2$: C, 31.3; H, 2.1; F, 59.4; N, 7.3%; M, 384), b.p. 153 °C/748 mmHg. IR $\nu_{max.}$ (cm^{-1}): 3330 and 3290 (m) (N–H str.); 1623 (s) (C=N str.); 1290–1180 (s) (C–F str.); 710 (s) (CF_3 def.). ^1H NMR (neat) δ: 7.06 (b, 1H, NH); 4.58 (mult., 2H, $=CH_2$); 2.55 (s, 2H, CH_2); 1.41 (s, 3H, CH_3) ppm. ^{19}F NMR δ: +11.4 [qd, 3F, $CF_3C=N$ (*syn*), $J=6$ and 2 Hz); +9.4 [q, 3F, $CF_3C=N$ (*anti*), $J=6$ Hz]; +3.7 [s, 6F, $(CF_3)_2C$] ppm. MS *m/z*: 384 (15.5%, M^+); 315 [34.7, $(M-CF_3)^+$]; 159 (14.7, $C_4H_4F_5^+$); 145 (35.0, $C_4H_2F_5^+$); 137 (18.4, $C_6H_8F_3^+$); 96 (18.1, $C_2HF_3N^+$); 69 (42.2, CF_3^+); 61 (100.0, $C_3H_6F^+$); 55 (96.7, $C_4H_7^+$); 42 (13.0, $C_3H_6^+$).

Component B was identified as 7-chloro-8,8,8-trifluoro-2-methyl-4,4,7-tris(trifluoromethyl)-5,6-diazaocta-1,5-diene (**6**) (nc) (0.31 g, 0.75 mmol, 11%) (Analysis: Found: C, 28.8; H, 1.6; Cl, 8.6; F, 54.4; N, 6.8%. $C_{10}H_7ClF_6N_2$ requires; C, 28.7; H, 1.7; Cl, 8.5; F, 54.5; N, 6.7%), b.p. 121 °C/744 mmHg. IR $\nu_{max.}$ (cm^{-1}): 1655 (m) (C=C str.); 1570 (w) (N=N str.); 1280–1230 (s) (C–F str.); 750 (s) (CF_3 def.). ^1H NMR (neat) δ: 4.60 and 4.56 (2s, 2H, $=CH_2$); 2.67 (s, 2H, CH_2); 1.24 (s, 3H, CH_3) ppm. ^{19}F NMR δ: +7.0 [s, 6F, $(CF_3)_2CCl$]; +4.2 [s, 6F, $(CF_3)_2C$] ppm. MS *m/z*: 390 and 392 [7.0%, $(M-N_2)^+$]; 245 and 247 (23.7, $C_6H_5ClF_7^+$); 226 and 228 (42.3, $C_6H_5ClF_6^+$); 205 (29.3, $C_7H_7F_6^+$); 185 (28.2, $C_7H_6F_5^+$); 171 and 173 (26.6, $C_6H_7ClF_3^+$); 145 (100.0, $C_4H_2F_5^+$); 95 (25.3, $C_3H_2F_3^+$); 77 (26.2, $C_3H_3F_2^+$); 75 (32.2, $C_3HF_2^+$); 73 (76.8, $C_4H_6F^+$); 69 (55.6, CF_3^+); 51 (25.4, $C_4H_3^+$); 41 (73.1, $C_3H_5^+$).

Component C was identified as 7-chloro-2-chloromethyl-8,8,8-trifluoro-4,4,7-tris(trifluoromethyl)-5,6-diazaocta-1,5-diene (**7**) (nc) (0.80 g, 1.76 mmol, 26%) (Analysis: Found: C, 26.8; H, 1.3; Cl, 15.3; F, 50.3; N, 6.0%. $C_{10}H_6Cl_2F_{12}N_2$ requires: C, 26.5; H, 1.3; Cl, 15.7; F, 50.3; N, 6.2%). IR $\nu_{max.}$ (cm^{-1}): 1645 (w) (C=C str.); 1572 (w) (N=N str.); 1290–1180 (s) (C–F str.); 740 and 730 (s) (CF_3 def.). ^1H NMR (neat) δ: 4.92 and 4.72 (2s, 2H, $=CH_2$); 3.45 (s, 2H, CH_2Cl); 2.83 (s, 2H, CH_2) ppm. ^{19}F NMR δ: +7.5 [s, 6F, $(CF_3)_2CCl$]; +4.2 [s, 6F, $(CF_3)_2C$] ppm. MS *m/z*: 424 and 426 [18.2%; $(M-N_2)^+$]; 239 and 241 (100.0, $C_7H_6ClF_6^+$); 203 (31.9, $C_7H_5F_6^+$), 185 and 187 (12.4, $C_3ClF_6^+$); 183 (21.4, $C_4H_2F_7^+$); 145 (29.7, $C_4H_2F_5^+$); 109 (24.0, $C_4H_4F_3^+$); 107 (65.5, $C_4H_2F_3^+$); 95 (24.0, $C_3H_2F_3^+$);

91 and 93 (25.2, $C_4H_6Cl^+$); 75 and 77 (43.1, C_3H_4Cl); 69 (95.4, CF_3^+); 51 (19.4, $C_4H_3^+$).

The residue (1.47 g) [(Analysis: Found: C, 27.6; H, 2.8; F, 39.0; N, 9.2%), m.p. >350 °C. IR $\nu_{max.}$ (cm^{-1}): 1605 and 1600 (s) (C=N str.); 1250–1195 (s) (C–F str.); 728 (s) (CF_3 def.). ^{19}F NMR (acetone-d_6) δ: +3.5 (s) ppm. MS *m/z*: 236 (29.0%, $C_7H_{10}F_6N_2^+$); 221 (100.0, $C_6H_7F_6N_2^+$); 72 (10.8, $C_4H_5F^+$); 69 (7.8, CF_3^+); 57 (15.0, $C_3H_2F^+$); 56 (44.5, $C_4H_8^+$)] was not identified.

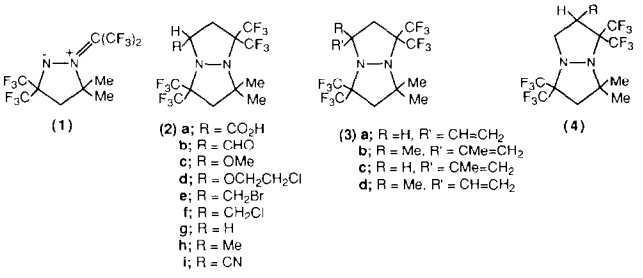
(l) With hydrogen chloride

A mixture of **1** (1.20 g, 3.13 mmol) and hydrogen chloride (0.08 g, 2.30 mmol), shaken at room temperature (7 d), gave unchanged hydrogen chloride (0.06 g, 1.64 mmol, 71% recovered) and a viscous yellow residue (1.21 g), which on fractional condensation *in vacuo* gave a 0 °C fraction (1.05 g). This material was shown (IR, ^1H and ^{19}F NMR spectroscopy and mass spectrometry) to consist of a 75:25 mixture of 8,8,8-trifluoro-2-methyl-4,4,7-tris(trifluoromethyl)-5,6-diaza-octa-1,6-diene (**5**) (*c.* 0.77 g, *c.* 2.0 mmol, *c.* 64%) and a compound tentatively identified as 7-chloro-1,1,1-trifluoro-7-methyl-2,5,5-tris(trifluoromethyl)-3,4-diaza-oct-3-ene (*c.* 0.28 g, *c.* 0.67 mmol, *c.* 21%). ^{19}F NMR δ: +8.3 [d, 6F $(CF_3)_2CH$, J = 7 Hz]; +7.2 [s, 6F, $(CF_3)_2C$] ppm.

Results and discussion

From the reaction of azomethinimine **1** with the monosubstituted ethenes CH_2=CHR (R = CO_2H, CHO, OMe, OCH_2CH_2Cl, CH_2Br and CH_2Cl) and the 1,3-dienes CH_2=CRCR=CH_2 (R = H and Me), a single [3+2] cycloadduct with the same regiochemistry was formed in each case in high yield (90%–98%). With isoprene, two adducts (ratio 64:36) were isolated resulting from regiospecific addition across the CH_2=CH– (major) and CH_2=CMe– groupings; favoured addition thus involved the less sterically bulky grouping.

In the ^1H NMR spectrum of the ethane adduct **2g**, triplet absorptions for the adjacent CH_2 groups were observed at δ 2.65 (CH_2–C) and 3.09 (CH_2–N) ppm [5, 11], and for the propane adduct **2b** the methylene protons (CH_2–C) absorbed at δ 2.50 ppm [12]. The methylene absorptions for the adducts prepared in the present work were in the range δ 2.2–3.0 ppm with the lowest field absorption observed for the acrylic acid adduct. If this compound had been the 3-substituted isomer **4** (R = CO_2H), the methylene (CH_2–N) proton absorption would have been expected at *c.* 0.4 ppm to lower field than the corresponding absorption in the ethane adduct **2g** (δ 3.09 ppm), i.e. at δ *c.* 3.5 ppm, because of deshielding by the CO_2H group. Furthermore, the methylene protons in the acrylonitrile adduct [5] also absorb at low field (AB, δ 3.46 and 3.12 ppm) and this compound was prepared (99%) and then pyrolysed at 200 °C to afford the alkene CH_2=$C(CF_3)_2$ (83%), thus establishing unequivocally that the adduct was the 2-substituted isomer **2i**. On the basis of this evidence, all the adducts are considered to be the 2-substituted diazabicyclo-octanes **2** and **3**; the 3-substituted isomers **4** were not detected.



Attempted cycloadditions of azomethinimine **1** across the C=N bond of phenyl isocyanate and the C=O bond of chloral were unsuccessful.

The only alkenes reported to undergo non-regiospecific addition with azomethinimine **1** are methyl and ethyl acrylate, which gave cycloadducts of types **2** and **4** in the ratio *c.* 95:5 [5], although the alkynes HC≡CCO_2Et and HC≡$CCH_2(CH_2)_nCH_3$ (n = 1, 2 and 3) also gave mixtures of the 2- and 3-substituted adducts in the ratios *c.* 50:50 and *c.* 85:15, respectively [5].

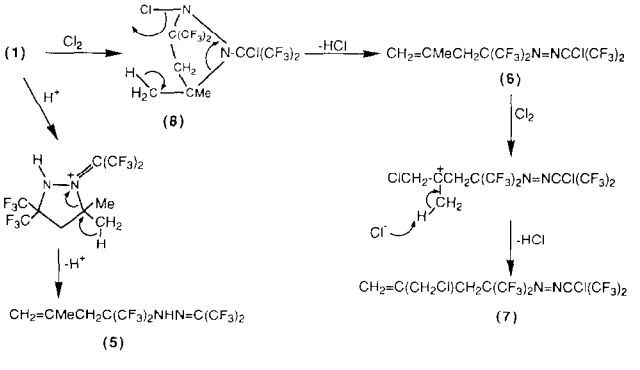
It was therefore decided to estimate the HOMO and LUMO energies of azomethinimine **1** to see if these data could be explained. Compound **1** is an azomethinimine of the general type $Z_2C=\overset{+}{N}R-\overset{-}{N}Z$ (where Z is an electron-withdrawing group and R is alkyl), and in order to estimate the HOMO and LUMO energies of **1** the effect of the substituents on the energies of the parent dipole $H_2C=\overset{+}{N}H-\overset{-}{N}H$ {HOMO, −8.6 eV; LUMO, +0.3 eV [13]} must be determined. Electron-withdrawing groups Z lower the energies of the HOMO and LUMO of ethene by 0.4 and 1.5 eV, respectively, while alkyl groups raise the energy of both the HOMO and LUMO by 1.5 eV [13]. From these values and values reported for the dipole coefficients at the sites of attachment of the substitutents [13], and using Houk's treatment [13], the HOMO and LUMO energies of azomethinimine **1** were calculated to be *c.* 9.7 eV and *c.* −1.0 eV, respectively.

However, before predictions of regiochemistry can be made, some estimation is required of the relative sizes of the coefficients ($C\beta^2/15$) at the termini of azomethinimine **1**. For the parent dipole, the values ($C\beta^2/15$) are HOMO (1.15) $CH_2=\overset{+}{N}H-\overset{-}{N}H$ (1.24) and LUMO (0.87) $CH_2=\overset{+}{N}H-\overset{-}{N}H$ (0.49) [13]. The major substituent difference between the parent dipole and azomethinimine **1** is the two CF_3 groups at the C-

terminus, which will reduce the coefficient at this position in both the HOMO and the LUMO. This leads to a greater polarisation of the coefficients in the HOMO (larger coefficient at N-terminus), while the larger coefficient in the LUMO would still be expected at the C-terminus. The $C(CF_3)_2$ group bonded to the N-terminus would be expected to slightly reduce the coefficient at nitrogen in both the HOMO and LUMO, thus increasing the coefficient difference in the LUMO and reducing it in the HOMO.

Overall, the larger coefficients would be expected at the N-terminus in the HOMO and at the C-terminus in the LUMO, as in the parent dipole. Therefore, reaction of **1** with alkenes $CH_2=CHR(X)(C)$ and alkynes $CH\equiv CR(C)$ (R = alkyl, X = mesomeric $+M$ groups, e.g. OR, NR_2, and C = conjugating groups, e.g. vinyl, Ph) would be expected to be LUMO–dipole controlled, leading to the 2-substituted cycloadducts, while in reaction with alkenes $CH_2=CHZ$ and alkynes $HC\equiv CZ$ (Z = electron-withdrawing $-M$ groups, e.g. CO_2R, COR) both LUMO–dipole and HOMO–dipole control could compete, leading to mixtures of the 2- and 3-substituted cycloadducts, as observed. The prediction that reaction with the alkynes $HC\equiv CR$ would lead to the 2-substituted cycloadducts only is contrary to observation. However, with alkynes a stronger HOMO–dipole control would be expected, leading to an increased possibility of formation of 3-substituted adducts, i.e. alkynes are less selective than alkenes.

The reaction of azomethinimine **1** with chlorine (*c.* 1:1 molar ratio) at room temperature (4 d) gave hydrogen chloride (61%), material soluble in CCl_4 which was separated (GLC) into its three components, dienes **5** (12%), **6** (11%) and **7** (26%), and unidentified material, m.p. >350 °C, which was insoluble in CCl_4 and was presumed to be polymeric. The products are considered to be formed as shown in Scheme 1.



Scheme 1.

It is considered that the reaction involves formation of the 1:1 adduct **8**, via chloronium-ion transfer to nitrogen followed by elimination of hydrogen chloride, involving a six-centre transition state which resulted in ring-opening to afford compound **6**. Further chloronium-ion transfer to the terminal carbon of the $-CMe=CH_2$ grouping in **6**, followed by proton loss, gave the dichlorodiene **7**. The hydrogen chloride formed then catalysed the ring-opening of azomethinimine **1** to the diene **5**. This latter compound has been reported to be formed by treatment of **1** with sulphur dioxide [8].

The results obtained from the reaction prompted an investigation of the reaction of **1** with hydrogen chloride. Reaction for an extended period at room temperature (7 d) using a 1:0.7 molar ratio of reactants, gave unchanged hydrogen chloride (71% recovered) and a mixture of diene **5** (*c.* 64%) and a compound containing a $(CF_3)_2CH$ group (^{19}F NMR spectroscopy). The amount of hydrogen chloride consumed is consistent with the formation of a 1:1 adduct (*c.* 21%), presumably of structure $(CF_3)_2CHN=NC(CF_3)_2CH_2CMe_2Cl$, which could arise by electrophilic addition of hydrogen chloride across the $-CMe=CH_2$ grouping in diene **5** and acid-catalysed tautomerism of the $(CF_3)_2C=NNH-$ grouping to $(CF_3)_2CHN=N-$.

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