

The reaction of perfluoro-2,5-diazahexane 2,5-dioxyl with alkenes

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Abstract

The liquid-phase reaction at room temperature of the title dioxyl (**1**) with an excess of the alkenes $\text{CH}_2=\text{CHR}$ ($\text{R}=\text{H}, \text{F}, \text{COCl}$), $\text{CF}_2=\text{CHF}$, $\text{CHCl}=\text{CCl}_2$ and *cis*- $\text{CHCl}=\text{CHCl}$ gives 1:1 copolymers **3** in high yield, although with the alkenes $\text{CH}_2=\text{CH}_2$, $\text{CH}_2=\text{CHF}$ and $\text{CF}_2=\text{CHF}$ cyclic 1:1 adducts **2** are also formed in low yield. The reactions with the alkenes $\text{CH}_2=\text{CMe}_2$, $\text{CH}_2=\text{CHEt}$, $\text{CH}_2=\text{CHCO}_2\text{H}$ and *cis*- $\text{HO}_2\text{CCH}=\text{CHCO}_2\text{H}$ produce copolymers which are not 1:1 copolymers. The 1:1 copolymer **3f** from acryloyl chloride is hydrolysed readily by water to the acrylic acid/dioxyl **1** 1:1 copolymer **3j**. Gas-phase reaction at room temperature of **1** with an excess of the alkenes $\text{CH}_2=\text{CHR}$ ($\text{R}=\text{Cl}, \text{Br}, \text{COCl}, \text{COF}$), $\text{CH}_2=\text{CXCH}_3$ ($\text{X}=\text{Cl}, \text{Br}$), $\text{CHCl}=\text{CCl}_2$, *cis*- and *trans*- $\text{CHCl}=\text{CHCl}$, $\text{CH}_2=\text{CCl}_2$, $\text{CF}_2=\text{CCl}_2$, $\text{CF}_2=\text{CFCl}$ and $\text{CF}_2=\text{CFBr}$ affords cyclic 1:1 adducts **2** (11.5–78%) and copolymers **3** (18.5–76.5%); hydrolysis of the acryloyl fluoride 1:1 adduct **2j** gives the acrylic acid 1:1 adduct **2s** in high yield.

Introduction

The chemistry of bis(trifluoromethyl)amino-oxyl, $(\text{CF}_3)_2\text{NO}\cdot$, has been studied in detail, but the reported reactions of its bifunctional analogue perfluoro-2,5-diazahexane 2,5-dioxyl (**1**) are very limited [1–6]. With compounds with which the oxyl $(\text{CF}_3)_2\text{NO}\cdot$ undergoes reaction to give 2:1 adducts, the dioxyl **1** forms heterocyclic compounds, e.g. with SO_2 [6], or copolymers or mixtures of copolymers and heterocyclic compounds, e.g. with fluoroalkenes [1, 2]. It has been reported that in the reactions of **1** with hexafluoropropene [2] and tetrafluoroethene [2, 7], copolymer formation was favoured by liquid-phase reaction and the production of 1:1 cycloadducts was favoured in the gas phase. Few reactions of dioxyl **1** have been carried out with alkenes containing hydrogen or with the object of preparing cyclic 1:1 adducts. In the present work, the scope of 1:1 cycloadduct formation has been investigated using fluoroalkenes and a wide variety of hydrogen-containing alkenes.

Experimental

Starting materials

Perfluoro-2,5-diazahexane 2,5-dioxyl (**1**) was prepared by hydrolysis of the 2:1:1 adduct formed from the

reaction of trifluoronitrosomethane with tetrafluoroethene and phosphorus trichloride followed by oxidation with potassium permanganate in dilute sulphuric acid [2]. Acryloyl chloride was made by reaction of acrylic acid with thionyl chloride at 60 °C and converted into acryloyl fluoride by reaction with an excess of antimony(III) fluoride under reflux. The remaining alkenes were either commercial samples or research samples available in the department and their purities were checked before use.

General techniques

Liquid-phase reactions were carried out at room temperature *in vacuo* in Rotaflo tubes (c. 300 cm³), while for gas-phase reactions the dioxyl **1** and the appropriate alkene were expanded separately into an evacuated Pyrex bulb (c. 10 dm³ unless stated otherwise) fitted with a Rotaflo tap. The tubes and bulbs were stored in the dark at room temperature until the purple colour of the dioxyl had disappeared. The volatile products were fractionated by passing the vapour at low pressure (1–2 mmHg) through traps cooled to an increasingly lower temperature, and the polymeric materials were extracted from the reaction vessels with 1,1,2-trichlorotrifluoroethane or acetone followed by removal of the solvent *in vacuo* and pumping to constant weight.

The products were examined by IR spectroscopy (Perkin-Elmer 137 or 257 instruments), ¹H NMR [Perkin-Elmer R10 (60.0 MHz) spectrometer; external

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reference Me₄Si] and ¹⁹F NMR spectroscopy [Perkin-Elmer R10 (56.46 MHz) or Varian Associates HA 100 (94.12 MHz) instruments, external reference trifluoroacetic acid (TFA)] and mass spectrometry (A.E.I. MS902 spectrometer with an electron beam energy of 70 eV). The NMR spectra were recorded using neat liquids or solutions (in CF₂ClCFCl₂ or Me₂CO) as stated in the text; 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 perfluoro-2,5-diazahexane 2,5-dioxy (1)

A. Liquid-phase reactions

(a) *With trifluoroethene* – A mixture of **1** (1.00 g, 3.36 mmol) and trifluoroethene (0.44 g, 5.37 mmol) on reaction (16 h) gave (i) a volatile mixture of unchanged trifluoroethene (0.16 g, 1.95 mmol, 36% recovered) (–196 °C fraction) and 3,3,4,4,7,7,8-heptafluoro-2,5-bis(trifluoromethyl)-1,6-dioxa-2,5-diazacyclo-octane (**2a**) (trace) (Analysis: Found: M⁺, 380. Calc. for C₆HF₁₃N₂O₂: M, 380) (–23 °C fraction). IR (ν_{max}) (cm⁻¹): 1284–1130 (vs) (C–F str.); 1099 (s) (C–O str.); 1065 (m) (N–O str.); and 710 (m) (CF₃ def.). MS *m/z*: 380 (15.8%, M⁺); 361 [34.7, (M–F)⁺]; 199 (55.8, C₃F₇NO⁺); 162 (35.9, C₃HF₅NO⁺); 133 (27.9, C₂F₅N⁺); 114 (28.3, C₂F₄N⁺); 100 (54.2, C₂F₄⁺); 99 (26.1, CF₃NO⁺); 82 (14.4, C₂HF₃⁺); and 69 (100.0, CF₃⁺), and (ii) a non-volatile viscous liquid which was identified as a 1:1 dioxy 1/trifluoroethene copolymer **3a** (nc) (1.15 g, 90%). [Analysis: Found: C, 19.2; H, 0.4; F, 64.5; N, 7.4%. (C₆HF₁₃N₂O₂)_n requires: C, 18.95; H, 0.3; F, 65.0; N, 7.4%.] IR (ν_{max}) (cm⁻¹): 1285–1210 (vs) (C–F str.); 1095 (s) (C–O str.); 1070 (s) (N–O str.); and 708 (m) (CF₃ def.). ¹H NMR (CF₂ClCFCl₂) δ: 6.31 [d, OCHF, J_{F–H (gem.)} = 55.8 Hz] ppm. ¹⁹F NMR δ: +12.0 (br., 6F, 2NCF₃); –12.3 (s, 2F, OCF₂); –21.9 (s, 2F, NCF₂); –23.0 (s, 2F, NCF₂); and –66.0 (d, 1F, CHF, J = 55.8 Hz) ppm. MS *m/z*: 773 (0.1%, C₁₃H₃F₂₆N₄O₄⁺); 760 (1.4, C₁₂H₂F₂₆N₄O₄⁺); 741 (8.2, C₁₂H₂F₂₅N₄O₄⁺); 361 (5.4, C₆HF₁₂N₂O₂⁺); 199 (11.4, C₃F₇NO⁺); 162 (16.4, C₃HF₅NO⁺); 149 (21.2, C₂F₅NO⁺); 133 (43.2, C₂F₅N⁺); 114 (41.4, C₂F₄N⁺); and 69 (100.0, CF₃⁺).

(b) *With vinyl fluoride* – A mixture of **1** (0.70 g, 2.35 mmol) and vinyl fluoride (0.12 g, 2.68 mmol) after storage (11 d) gave (i) unchanged vinyl fluoride (0.04 g, 0.74 mmol), contaminated with small amounts of trifluoronitrosomethane and perfluoro-2-azapropene (IR) (–196 °C fraction), (ii) 3,3,4,4,7-pentafluoro-2,5-bis(trifluoromethyl)-1,6-dioxa-2,5-diazacyclo-octane (**2b**) (0.03 g, 0.09 mmol, 4%) (Analysis: Found: M⁺, 344. Calc. for C₆H₃F₁₁N₂O₂: M, 344) (–23 °C fraction). IR (ν_{max}) (cm⁻¹): 2899 and 2809 (w) (C–H str.); 1276–1135

(vs) (C–F str.); 1087 (s) (C–O str.); and 1054 (m) (N–O str.). MS *m/z*: 344 (1.5%, M⁺); 235 [7.8, (M–F)⁺]; 153 (10.6, C₄H₂F₃NO₂⁺); 151 (17.0, C₄H₂F₃N₂O⁺); 149 (24.5, C₂F₅NO⁺); 114 (21.1, C₂F₄N⁺); 103 (16.3, C₃H₂FNO₂⁺); 101 (21.9, C₃H₂FN₂O⁺); 69 (100.0, CF₃⁺); and 44 (54.7, C₂HF⁺), and (iii) a non-volatile viscous liquid identified as a 1:1 dioxy 1/vinyl fluoride copolymer **3b** (nc) (0.77 g, 95%). [Analysis: Found: C, 20.8; H, 1.1; F, 60.3; N, 7.8%. (C₆H₃F₁₁N₂O₂)_n requires: C, 20.9; H, 0.9; F, 60.8; N, 8.1%.] IR (ν_{max}) (cm⁻¹): 1272–1171 (vs) (C–F str.); 1095 (s) (C–O str.); 1058 (s) (N–O str.); and 702 (s) (CF₃ def.). ¹H NMR (CF₂ClCFCl₂) δ: 6.37 [d mult., 1H, OCHF, J_{F–H (gem.)} = 60.0 Hz]; and 4.91 (d, 2H, OCH₂, J = 6.6 Hz) ppm. ¹⁹F NMR δ: +12.6 (s, 3F, NCF₃); +11.9 (mult., 3F, NCF₃); –23.6 (s, 2F, CF₂N); –24.9 (mult., 2F, CF₂N); and –56.6 (d, 1F, CHF, J = 60.0 Hz) ppm. MS *m/z*: 688 (7.1%, C₁₂H₆F₂₂N₄O₂⁺); 325 (9.2, C₆H₃F₁₀O₂⁺); 309 (15.1, C₆H₃F₁₀N₂O⁺); 164 (12.1, C₃F₆N⁺); 151 (14.8, C₄H₂F₃N₂O⁺); 149 (50.1, C₂F₅NO⁺); 134 (21.4, C₂HF₅N⁺); 114 (52.2, C₂F₄N⁺); 100 (18.0, C₂F₄⁺); 69 (100.0, CF₃⁺); 62 (29.3, C₂H₃FO⁺); 61 (21.2, C₂H₂FO⁺); and 44 (20.0, CH₂NO⁺).

(c) *With vinylidene fluoride* – A mixture of **1** (0.77 g, 2.58 mmol) and vinylidene fluoride (0.225 g, 3.50 mmol) after storage (21 d) gave (i) unchanged vinylidene fluoride (0.06 g, 0.91 mmol, 26% recovered) which condensed at –196 °C, (ii) 3,3,4,4,7,7-hexafluoro-2,5-bis(trifluoromethyl)-1,6-dioxa-2,5-diazacyclo-octane (**2c**) (0.03 g, 0.08 mmol, 3%) (Analysis: Found: M⁺, 362. Calc. for C₆H₂F₁₂N₂O₂: M, 362) which condensed at –23 °C and was identified by a comparison of its ¹H and ¹⁹F NMR spectra with those obtained previously [8], and (iii) a 1:1 dioxy 1/vinylidene fluoride copolymer **3c** (0.85 g, 91%). [Analysis: Found: C, 19.9; H, 0.6; F, 62.7; N, 7.7%. Calc. for (C₆H₂F₁₂N₂O₂)_n: C, 19.9; H, 0.6; F, 63.0; N, 7.7%.] The ¹H, ¹⁹F NMR and mass spectra of the latter were identical to those recorded previously [8].

(d) *With trichloroethene* – A mixture of **1** (0.66 g, 2.21 mmol) and trichloroethene (0.61 g, 4.64 mmol), during 0.5 h gave unchanged alkene (0.32 g, 2.43 mmol, 52% recovered) and a non-volatile viscous liquid which was identified as a 1:1 dioxy 1/trichloroethene copolymer **3d** (nc) (0.91 g, 96%) [Analysis: Found: C, 16.8; H, 0.5; Cl, 24.6; F, 44.4%. (C₆HCl₃F₁₀N₂O₂)_n requires: C, 16.8; H, 0.2; Cl, 24.8; F, 44.2%.] IR (ν_{max}) (cm⁻¹): 1280–1189 (vs) (C–F str.); 1106 (m) (C–O str.); 1041 (s) (N–O str.); and 703 (m) (CF₃ def.). ¹H NMR (CF₂ClCFCl₂) δ: 6.72 (s, OCHCl) ppm. ¹⁹F NMR δ: +14.6 (mult., 3F, NCF₃); +13.4 (mult., 3F, NCF₃); and –18.0 (mult., 4F, CF₂CF₂) ppm. MS *m/z*: 850 (0.1%, C₁₃H₃Cl₆F₁₉N₄O₄⁺); 393/395/397 (12.3,

$C_6HCl_2F_{10}N_2O_2^+$); 199 (34.6, $C_3F_7NO^+$); 151/153 (65.8, $C_3HClFN_2O_2^+$); 149 (71.7, $C_2F_5NO^+$); 130/132 (51.7, $C_2HCl_3^+$); 114 (26.0, $C_2F_4N^+$); 101/103 (86.0, C_3ClNO^+); 69 (100.0, CF_3^+); and 63/65 (17.2, $CClO^+$).

(e) *With (Z)-1,2-dichloroethane* – A mixture of **1** (0.53 g, 1.78 mmol) and the alkene (0.30 g, 3.09 mmol) when stored (48 h) gave unchanged alkene (0.13 g, 1.31 mmol, 42.5% recovered) and a non-volatile viscous liquid identified as a 1:1 dioyl 1/1,2-dichloroethane copolymer **3e** (nc) (0.70 g, 99.5%). [Analysis: Found: C, 18.2; H, 0.7; F, 48.0; N, 6.9%; M, 2943. ($C_6H_2Cl_2F_{10}N_2O_2$)_n requires: C, 18.2; H, 0.5; F, 48.1; N, 7.1%.] IR (ν_{max}) (cm^{-1}): 3049 (w) (C–H str.); 1300–1193 (vs) (C–F str.); 1075 (m) (C–O str.); 1034 (s) (N–O str.); and 732 (s) (CF_3 def.). 1H NMR ($CF_2ClCFCl_2$) δ : 6.66 (s, $CHClCHCl$) ppm. ^{19}F NMR δ : +13.5 (s, 6F, $2NCF_3$); and –20.1 (s, 4F, CF_2CF_2) ppm. MS m/z : 751 (0.6%, $C_{12}H_3Cl_4F_{18}N_4O_4^+$); 622 (1.4, $C_{10}H_2F_{20}N_4O_4^+$); 359/361 (16.2, $C_6H_2ClF_{10}N_2O_2^+$); 149 (23.3, $C_2F_5NO^+$); 114 (39.4, $C_2F_4N^+$); 111/113/115 (30.2, $C_2HCl_2O^+$); 77/79 (14.2, $C_2H_2ClO^+$); 69 (100.0, CF_3^+); and 49/51 (15.7, CH_2Cl^+).

(f) *With acryloyl chloride* – A mixture of **1** (0.41 g, 1.38 mmol) and acryloyl chloride (0.25 g, 2.76 mmol) during 30 min gave unchanged acryloyl chloride (0.13 g, 1.44 mmol, 52% recovered) and a viscous liquid identified as a 1:1 dioyl 1/acryloyl chloride copolymer **3f** (nc) (0.53 g, 98.5%) [Analysis: Found: C, 21.5; H, 0.8; F, 48.7%. ($C_7H_3ClF_{10}N_2O_3$)_n requires: C, 21.6; H, 0.8; F, 48.9%.] IR (ν_{max}) (cm^{-1}): 1792 (m) (C=O str.); 1270–1170 (vs) (C–F str.); 1024 (s) (C–O and/or N–O str.); and 710 (m) (CF_3 def.). 1H NMR ($CF_2ClCFCl_2$) δ : 4.92 (mult., 1H, CH); and 4.55 (mult., 2H, CH_2) ppm. ^{19}F NMR δ : +12.3 (mult., 3F, NCF_3); +11.9 (mult., 3F, NCF_3); –21.4 (br., 2F, CF_2); and –24.9 (mult., 2F, CF_2) ppm. MS m/z : 353 (1.2%, $C_7H_3F_{10}N_2O_3^+$); 325 (8.0, $C_6H_3F_{10}N_2O_2^+$); 151/153 (21.1, $C_3HClFN_2O_2^+$); 114 (42.1, $C_2F_4N^+$); 101/103 (30.4, C_3ClNO^+); 77/79 (12.3, $C_2H_2ClO^+$); 69 (100.0, CF_3^+); and 29 (28.6, CHO^+).

(g) *With ethene* – A mixture of **1** (0.79 g, 2.65 mmol) and ethene (0.105 g, 3.75 mmol) on reaction (5 d) gave (i) unchanged ethene (0.03 g, 1.07 mmol, 28.5% recovered) which condensed at –196 °C, (ii) 3,3,4,4-tetrafluoro-2,5-bis(trifluoromethyl)-1,6-dioxo-2,5-diazacyclo-octane (**2d**) (trace) (Analysis: Found: M^+ , 326. Calc. for $C_6H_4F_{10}N_2O_2$: M, 326) which condensed at –23 °C, and (iii) a 1:1 dioyl 1/ethene copolymer (**3g**) (0.79 g, 91%). [Analysis: Found: C, 21.8; H, 1.3; N, 8.5%. Calc. for ($C_6H_4F_{10}N_2O_2$)_n: C, 22.1; H, 1.2; N, 8.6%.] IR (ν_{max}) (cm^{-1}): 3390 and 3279 (w) (O–H str.); and 1835 (w) (C=O str.). The 1H and ^{19}F NMR

spectra of the latter were identical to those recorded previously [7].

(h) *With 2-methylpropene* – A mixture of **1** (1.69 g, 5.67 mmol) and 2-methylpropene (0.385 g, 6.87 mmol) during 10 min gave (i) unchanged alkene (0.02 g, 0.36 mmol, 5% recovered) (–140 °C fraction), (ii) a colourless gas (0.08 g, 1.31 mmol) (Analysis: Found: M, 61) which condensed at –96 °C and was shown (IR) to be 2-methylpropene contaminated with unidentified fluorinated material, and (iii) a viscous liquid considered to be a dioyl 1/2-methylpropene copolymer (1.92 g, 97% by weight). [Analysis: Found: C, 25.8; H, 2.0; N, 7.8%; M, 2592. Calc. for ($C_8H_8F_{10}N_2O_2$)_n: C, 27.1; H, 2.3; N, 7.9%.] IR (ν_{max}) (cm^{-1}): 3472 (m) (O–H str.); 2976 (w) (C–H str.); 1815 (m) (C=O or C=C str.); 1333–1149 (vs) (C–F str.); 1044 (s) (N–O str.); and 705 (m) (CF_3 def.).

A second reaction carried out between dioyl **1** (0.87 g, 2.92 mmol) and 2-methylpropene (0.245 g, 4.37 mmol) at –78 °C (24 h) gave unchanged 2-methylpropene (0.05 g, 0.97 mmol, 22% recovered) and a dioyl 1/2-methylpropene copolymer (0.99 g, 93% by weight). [Analysis: Found: C, 25.7; H, 2.0; N, 7.9%; M, 1653].

(i) *With but-1-ene* – A mixture of **1** (0.77 g, 2.58 mmol) and but-1-ene (0.20 g, 3.57 mmol) during 25 min gave (i) unchanged but-1-ene (0.13 g, 2.32 mmol, 65% recovered) which condensed at –196 °C, (ii) a colourless liquid (0.09 g), IR (ν_{max}) (cm^{-1}): 2995 (m) (C–H str.); 1830 (m) (C=N str.); 1220 (s) C–F str.; and 1025 (s) (Si–F str.), which condensed at –23 °C, and (iii) a dioyl 1/but-1-ene copolymer (0.70 g, 93% by weight). [Analysis: Found: C, 24.1; H, 1.7; N, 8.1%. Calc. for ($C_8H_8F_{10}N_2O_2$)_n: C, 27.1; H, 2.3; N, 7.9%.] IR (ν_{max}) (cm^{-1}): 3559 and 3333 (m) (O–H str.); 1773 and 1669 (m) (C=O or C=C str.); 1350–1140 (vs) (C–F str.); 1044 (s) (N–O str.); and 708 (s) (CF_3 def.).

(j) *With acrylic acid* – A mixture of acrylic acid (0.235 g, 3.26 mmol) and **1** (0.85 g, 2.85 mmol) when stored for 3 weeks gave (i) a colourless gas (0.06 g, 0.60 mmol) which was shown (IR) to be a mixture of trifluoronitrosomethane, perfluoro-2-azapropene, trifluoromethylisocyanate and tetrafluorosilane, and (ii) a white rubbery solid (removed with acetone) which was considered and shown to be a dioyl 1/acrylic acid copolymer (1.02 g). [Analysis: Found: C, 24.3; H, 2.0; N, 7.3%. Calc. for ($C_7H_4F_{10}N_2O_4$)_n: C, 22.7; H, 1.1; N, 7.6%.] IR (ν_{max}) (cm^{-1}): 3335–2898 (br.) (O–H str. and C–H str.); 1724 (s) (C=O str.); 1290–1160 (vs) (C–F str.); 1073 (s) (C–O str.); 1049 (s) (N–O str.); and 705 (m) (CF_3 def.).

(k) *With maleic acid* – A mixture of **1** (1.35 g, 4.53 mmol), maleic acid (0.48 g, 4.14 mmol), water (5.5 cm³) and 1,1,2-trichlorotrifluoroethane (5 cm³) when heated at 52 °C (31 h) gave a volatile material which was removed *in vacuo* and a viscous non-volatile liquid which was considered to be a dioxy **1**/maleic acid copolymer (1.00 g). [Analysis: Found: C, 23.8; H, 2.8; F, 32.7%. Calc. for (C₈H₄F₁₀N₂O₆)_n: C, 23.2; H, 1.0; F, 45.9%.] IR (ν_{\max}) (cm⁻¹): 3390 (s) (O–H str.); 1712 (s) (C=O str.); 1635 (s) (C=N str.?); 1280–1175 (vs) (C–F str.); 1055 (m) (C–O and/or N–O str.); and 720 (m) (CF₃ def.).

B. Gas-phase reactions

(a) *With 1,1-dichloroethene* – A mixture of **1** (1.12 g, 3.76 mmol) and the alkene (0.56 g, 5.78 mmol), stored in a bulb (5 dm³, 3 d), gave unchanged alkene (0.23 g, 2.37 mmol, 41% recovered) and 3,3,4,4-tetrafluoro-7,7-dichloro-2,5-bis(trifluoromethyl)-1,6-dioxo-2,5-diazacyclo-octane (**2g**) (nc) (0.51 g, 1.29 mmol, 34.5%) (Analysis: Found: C, 18.3; H, 0.7; F, 47.9; N, 7.0%; M⁺, 394/396/398. C₆H₂Cl₂F₁₀N₂O₂ requires C, 18.2; H, 0.5; F, 48.1; N, 7.1%, M, 395), b.p. 157 °C, n_D^{20} 1.3589. IR (ν_{\max}) (cm⁻¹): 2967 (w) (C–H str.); 1279–1195 (vs) (C–F str.); 1080 (s) (C–O str.); 1058 (s) (N–O str.); 980 (m) (C–N str.); and 708 (s) (CF₃ def.). ¹H NMR (neat) δ : 5.22 (s, CH₂) ppm. ¹⁹F NMR δ : +14.1 (t, 3F, CF₃N–OCCL₂, J =14.1 Hz); +11.0 (t, 3F, CF₃N–OCH₂, J =13.0 Hz); and –28.0 (mult., 4F, CF₂CF₂) ppm. MS m/z : 394/396/398 (1.8%, M⁺); 359/361 [43.9, (M–Cl)⁺]; 199 (20.9, C₃F₇NO⁺); 149 (40.0, C₂F₅NO⁺); 114 (42.1, C₂F₄N⁺); 111/113/115 (96.2, C₂HCl₂O⁺); 100 (38.8, C₂F₄⁺); 69 (100.0, CF₃⁺); and 49/51 (49.0, CH₂Cl⁺). In addition, 1:1 dioxy **1**/1,1-dichloroethene copolymer (**3k**) (nc) (0.91 g, 61.5%) was obtained. [Analysis: Found: C, 18.4; H, 0.7; F, 48.2; N, 7.1%. (C₆H₂Cl₂F₁₀N₂O₂)_n requires: C, 18.2; H, 0.5; F, 48.1; N, 7.1%.] IR (ν_{\max}) (cm⁻¹): 1272–1189 (vs) (C–F str.); 1079 (s) (C–O str.); 1057 (s) (N–O str.); and 714 (m) (CF₃ def.). ¹H NMR (CF₂ClCFCl₂) δ : 5.27 (s, CH₂) ppm. ¹⁹F NMR δ : +14.0 (mult., 3F, CF₃N–OCCL₂); +11.8 (mult., 3F, CF₃N–OCH₂); –18.0 (mult., 2F, CF₂); and –24.5 (mult., 2F, CF₂) ppm. MS m/z : 753/755 (0.4%, C₁₂H₄Cl₃F₂₀N₄O₄⁺); 359/361 (16.0, C₆H₂ClF₁₀N₂O₂⁺); 150 (25.9, C₂HF₅NO⁺); 149 (34.5, C₂F₅NO⁺); 114 (42.0, C₂F₄N⁺); 111/113/115 (98.5, C₂HCl₂O⁺); 100 (21.4, C₂F₄⁺); 85 (19.2, C₂HN₂O₂⁺); 77/79 (16.0, C₂H₂ClO⁺); 69 (100.0, CF₃⁺); and 49/51 (32.7, CH₂Cl⁺).

Five further experiments were carried out (10 dm³ bulb) when the following results were obtained.

(i) A mixture of **1** (0.73 g, 2.45 mmol) and the alkene (0.34 g, 3.50 mmol) when stored (6 d) gave the unchanged alkene (0.25 g, 1.24 mmol, 35.5% recovered), **2g** (0.54 g, 1.37 mmol, 56%) and **3k** (0.42 g, 43.5%).

(ii) A mixture of **1** (1.31 g, 4.40 mmol) and the alkene (0.49 g, 5.05 mmol) when stored (5 d) gave the unchanged alkene (0.07 g, 0.76 mmol, 15% recovered), **2g** (0.87 g, 2.20 mmol, 50%) and **3k** (0.76 g, 43.5%).

(iii) A mixture of **1** (1.29 g, 4.33 mmol) and the alkene (0.61 g, 6.29 mmol) when stored (4 d) gave the unchanged alkene (0.19 g, 1.96 mmol, 31% recovered), **2g** (0.85 g, 2.15 mmol, 49.5%) and **3k** (0.78 g, 45.5%).

(iv) A mixture of **1** (1.25 g, 4.19 mmol) and the alkene (0.65 g, 6.70 mmol) when stored (5 d) gave the unchanged alkene (0.225 g, 2.32 mmol, 34.5% recovered), **2g** (0.845 g, 2.14 mmol, 51%) and **3k** (0.76 g, 46%).

(v) A mixture of **1** (1.35 g, 4.53 mmol) and the alkene (0.87 g, 8.97 mmol) when stored (5 d) gave the unchanged alkene (0.43 g, 4.40 mmol, 45.5% recovered), **2g** (0.88 g, 2.23 mmol, 49%) and **3k** (0.83 g, 46.5%).

(b) *With vinyl chloride* – A mixture of **1** (1.33 g, 4.46 mmol) and the alkene (0.395 g, 6.32 mmol) when stored (56 d) gave a mixture (trace) of the compounds CF₃NO, CF₃NCO and CF₃N=CF₂ (IR), unchanged alkene (0.145 g, 2.32 mmol, 36.5% recovered) and 7-chloro-3,3,4,4-tetrafluoro-2,5-bis(trifluoromethyl)-1,6-dioxo-2,5-diazacyclo-octane (**2h**) (nc) (0.51 g, 1.41 mmol, 31.5%). (Analysis: Found: C, 19.9; H, 1.0; F, 52.5; N, 7.7%; M⁺, 360/362. C₆H₃ClF₁₀N₂O₂ requires: C, 20.0; H, 0.8; F, 52.7; N, 7.8%; M, 360.5), b.p. 149 °C, n_D^{20} 1.3411. IR (ν_{\max}) (cm⁻¹): 2959 (w) (C–H str.); 1275–1170 (vs) (C–F str.); 1080 (s) (C–O str.); 1067 and 1047 (s) (N–O str.); and 706 (s) (CF₃ def.). ¹H NMR (neat) δ : 6.47 (t, 1H, CHCl, J =6.6 Hz); and 4.83 (d, 2H, CH₂, J =6.6 Hz) ppm. ¹⁹F NMR δ : +11.2 (mult., 6F, 2CF₃N); and –26.5, –30.0, –36.9 and –40.6 (4 mult., 4F, CF₂CF₂) ppm. MS m/z : 360/362 (1.5%, M⁺); 341/343 [5.3, (M–F)⁺]; 325 [7.6, (M–Cl)⁺]; 149 (44.0, C₂F₅NO⁺); 114 (29.5, C₂F₄N⁺); 77/79 (22.9, C₂H₂ClO⁺); 69 (100.0, CF₃⁺); 49/51 (31.8, CH₂Cl⁺); and 30 (14.1, CH₂O⁺ and NO⁺). In addition, a 1:1 dioxy **1**/vinyl chloride copolymer (**3l**) (nc) (0.99 g, 61.5%) was obtained. [Analysis: Found: C, 20.1; H, 0.9; F, 52.5; N, 7.6%. (C₆H₃ClF₁₀N₂O₂)_n requires: C, 20.0; H, 0.8; F, 52.7; N, 7.8%.] IR (ν_{\max}) (cm⁻¹): 1271–1182 (vs) (C–F str.); 1074 (s) (C–O str.); 1052 (s) (N–O str.); and 716 and 704 (m) (CF₃ def.). ¹H NMR (CF₂ClCFCl₂) δ : 6.64 (t, 1H, CHCl, J =6.0 Hz); and 5.01 (mult., 2H, CH₂) ppm. ¹⁹F NMR δ : +13.5 (br., 3F, CF₃N–OCHCl); +11.9 (mult., 3F, CF₃N–OCH₂); –21.0 (br., 2F, CF₂); and –25.2 (mult., 2F, CF₂) ppm. MS m/z : 720/722 (0.9%, C₁₂H₆Cl₂F₂₀N₄O₄⁺); 359/361 (11.1, C₆H₂ClF₁₀N₂O₂⁺); 150 (15.0, C₂HF₅NO⁺); 149 (23.2, C₂F₅NO⁺); 134 (17.3, C₂HF₅N⁺); 114 (34.7, C₂F₄N⁺); 99 (19.1, CF₃NO⁺); 97 (28.9, C₂H₂F₃N⁺); 78/80 (28.7, C₂H₃ClO⁺); 77/79 (41.7, C₂H₂ClO⁺); 69

(100.0, CF_3^+); 49/51 (30.1, CH_2Cl^+); and 29 (30.2, CHO^+).

(c) *With vinyl bromide* – A mixture of **1** (1.18 g, 3.96 mmol) and the alkene (0.65 g, 6.07 mmol) when stored (35 d) gave a mixture (trace) of the compounds CF_3NO and CF_3NCO (IR), unchanged alkene (0.235 g, 2.20 mmol, 36% recovered) and 7-bromo-3,3,4,4-tetrafluoro-2,5-bis(trifluoromethyl)-1,6-dioxo-2,5-diazacyclo-octane (**2i**) (nc) (0.68 g, 1.68 mmol, 42.5%). (Analysis: Found: C, 18.1; H, 0.9; Br, 19.7; F, 46.9; N, 6.8%; M^+ , 404/406. $\text{C}_6\text{H}_3\text{BrF}_{10}\text{N}_2\text{O}_2$ requires: C, 17.8; H, 0.7; Br, 19.8; F, 46.9; N, 6.9%; M , 405), b.p. 150 °C, n_D^{20} 1.3560. IR (ν_{max}) (cm^{-1}): 2959 (w) (C–H str.); 1263–1168 (vs) (C–F str.); 1086 (s) (C–O str.); 1057 and 1046 (s) (N–O str.); and 707 (s) (CF_3 def.). ^1H NMR (neat) δ : 6.88 (t, 1H, CHBr , $J=6.6$ Hz); and 5.01 (d, 2H, CH_2 , $J=6.6$ Hz) ppm. ^{19}F NMR δ : +11.4 (mult., 6F, $2\text{CF}_3\text{N}$); and –26.5, –30.0, –37.0 and –40.5 (4 mult., 4F, CF_2CF_2) ppm. MS m/z : 404/406 (2.2%, M^+); 325 [14.4, ($M-\text{Br}$) $^+$]; 282 (8.7, $\text{C}_4\text{F}_{10}\text{N}_2\text{O}^+$); 149 (37.7, $\text{C}_2\text{F}_5\text{NO}^+$); 121/123 (15.0, $\text{C}_2\text{H}_2\text{BrO}^+$); 114 (27.5, $\text{C}_2\text{F}_4\text{N}^+$); 92/94 (16.8, CHBr^+); 69 (100.0, CF_3^+); and 29 (16.7, CHO^+). In addition, a 1:1 oxyl **1**/vinyl bromide copolymer (**3m**) (nc) (0.86 g, 53.5%) was obtained. [Analysis: Found: C, 18.1; H, 0.9; F, 46.9; N, 6.8%. ($\text{C}_6\text{H}_3\text{BrF}_{10}\text{N}_2\text{O}_2$) $_n$ requires: C, 17.8; H, 0.7; F, 46.9; N, 6.9%.] IR (ν_{max}) (cm^{-1}): 2941 (w) (C–H str.); 1285–1176 (vs) (C–F str.); 1063 and 1042 (s) (N–O str.); and 713 and 703 (s) (CF_3 def.). ^1H NMR ($\text{CF}_2\text{ClCFCl}_2$) δ : 6.77 (br., 1H, CHBr); and 5.08 (br., 2H, CH_2) ppm. ^{19}F NMR δ : +13.5 (s, 3F, $\text{CF}_3\text{N}-\text{OCHBr}$); +11.9 (s, 3F, CF_3NOCH_2); –20.8 (br., 2F, CF_2); and –25.2 (mult., 2F, CF_2) ppm. MS m/z : 729/731 (3.1%, $\text{C}_{12}\text{H}_6\text{BrF}_{20}\text{N}_4\text{O}_4^+$); 295 (7.9, $\text{C}_5\text{HF}_{10}\text{N}_2\text{O}^+$); 185/187 (10.8, $\text{C}_3\text{H}_2\text{BrF}_2\text{NO}^+$); 150 (16.6, $\text{C}_2\text{HF}_5\text{NO}^+$); 149 (25.6, $\text{C}_2\text{F}_5\text{NO}^+$); 134 (13.0, $\text{C}_2\text{HF}_5\text{N}^+$); 121/123 (17.2, $\text{C}_2\text{H}_2\text{BrO}^+$); 114 (30.4, $\text{C}_2\text{F}_4\text{N}^+$); 69 (100.0, CF_3^+); 43 (18.4, $\text{C}_2\text{H}_3\text{O}^+$); and 29 (41.5, CHO^+).

(d) *With acryloyl fluoride* – A mixture of **1** (1.50 g, 5.03 mmol) and the alkene (0.53 g, 7.16 mmol) when stored (42 d) gave tetrafluorosilane (0.05 g, 0.48 mmol), unchanged alkene (0.155 g, 2.09 mmol, 29% recovered) and 3,3,4,4-tetrafluoro-7-(fluoroformyl)-2,5-bis(trifluoromethyl)-1,6-dioxo-2,5-diazacyclo-octane (**2j**) (nc) (0.30 g, 0.81 mmol, 16%). IR (ν_{max}) (cm^{-1}): 2985 (w) (C–H str.); 1724 (m) (C=O str.); 1295–1166 (vs) (C–F str.); 1089 and 1076 (m) (C–O str.); 1053 and 1047 (s) (N–O str.); and 709 (s) (CF_3 def.). ^1H NMR (neat) δ : 5.07 (br., 1H, CH); and 4.46 (br., 2H, CH_2) ppm. ^{19}F NMR δ : +99.6 (s, 1F, COF); +11.0 (mult., 6F, $2\text{CF}_3\text{N}$); –26.8 and –30.1 (mult., 2F, CF_2-N); and –37.4 and 41.0 (mult., 2F, CF_2-N) ppm.

In addition, a dioxyl **1**/acryloyl fluoride copolymer (1.45 g, c. 77%) was obtained. [Analysis: Found: C, 24.0; H, 1.4; F, 51.5%. Calc. for ($\text{C}_7\text{H}_3\text{F}_{11}\text{N}_2\text{O}_3$) $_n$: C, 22.6; H, 0.8; F, 56.2%.] IR (ν_{max}) (cm^{-1}): 2976 (m) (C–H str.); 1880 and 1859 (s) (C=O str.); 1351–1020 (vs) (C–F, C–O and N–O str.); and 705 (s) CF_3 def.).

The cyclo-octane **2j** on storage rapidly changed to a white solid, presumed to be the corresponding carboxylic acid formed by hydrolysis.

(e) *With acryloyl chloride* – A mixture of **1** (1.50 g, 5.03 mmol) and the alkene (0.51 g, 5.64 mmol) when stored (21 d) gave a mixture of unchanged alkene and an unidentified material (0.09 g, 1.33 mmol) and 7-(chloroformyl)-3,3,4,4-tetrafluoro-2,5-bis(trifluoromethyl)-1,6-dioxo-2,5-diazacyclo-octane (**2k**) (nc) (0.23 g, 0.59 mmol, 11.5%). [Analysis: Found: C, 21.8; H, 1.1%. $\text{C}_7\text{H}_3\text{ClF}_{10}\text{N}_2\text{O}_3$ requires: C, 21.6; H, 0.8%.] IR (ν_{max}) (cm^{-1}): 2967 (w) (C–H str.); 1800 (m) (C=O str.); 1286–1170 (vs) (C–F str.); 1082 (s) (C–O str.); 1050 (s) (N–O str.); and 708 (s) (CF_3 def.). ^1H NMR (neat) δ : 5.03 (mult., 1H, CH); and 4.44 (mult., 2H, CH_2) ppm. ^{19}F NMR δ : +11.2 (mult., 6F, $2\text{CF}_3\text{N}$); –26.6 and –29.8 (2 mult., 2F, CF_2); and –37.0 and –40.6 (2 mult., 2F, CF_2) ppm. MS m/z : 325 [4.1, ($M-\text{COCl}$) $^+$]; 149 (8.1, $\text{C}_2\text{F}_5\text{NO}^+$); 114 (29.1, $\text{C}_2\text{F}_4\text{N}^+$); 69 (100.0, CF_3^+); 63/65 (9.9, CClO^+); 43 (9.2, $\text{C}_2\text{H}_3\text{O}^+$); and 29 (37.0, CHO^+). In addition, a 1:1 dioxyl **1**/acryloyl chloride copolymer **3f** (1.46 g, 75%) was obtained. [Analysis: Found: C, 21.6; H, 0.8; F, 49.4%. Calc. for ($\text{C}_7\text{H}_3\text{ClF}_{10}\text{N}_2\text{O}_3$) $_n$: C, 21.6; H, 0.8; F, 48.9%].

(f) *With 2-chloropropene* – A mixture of **1** (1.08 g, 2.63 mmol) and the alkene (0.435 g, 5.69 mmol) when stored (3 d) gave unchanged alkene (0.15 g, 1.96 mmol, 34.5% recovered) and 7-chloro-3,3,4,4-tetrafluoro-7-methyl-2,5-bis(trifluoromethyl)-1,6-dioxo-2,5-diazacyclo-octane (**2l**) (nc) (0.32 g, 0.85 mmol, 23.5%). (Analysis: Found: C, 22.0; H, 1.4; Cl, 9.4; F, 51.0; N, 7.2%; M^+ , 374/376. $\text{C}_7\text{H}_5\text{ClF}_{10}\text{N}_2\text{O}_2$ requires: C, 22.4; H, 1.3; Cl, 9.5; F, 50.7; N, 7.5%; M , 374.5), b.p. 153 °C, n_D^{20} 1.3482. IR (ν_{max}) (cm^{-1}): 2959 (w) (C–H str.); 1265–1169 (vs) (C–F str.); 1082 (s) C–O str.); 1064 and 1040 (m) (N–O str.); and 709 (s) (CF_3 def.). ^1H NMR (neat) δ : 5.25 and 4.89 (AB, 2H, CH_AH_B , $J=13.8$ Hz); and 2.48 (s, 3H, CH_3) ppm for conformer A and 4.83 (br., 0.67H, CH_2); and 2.62 (s, 1.0H, CH_3) ppm for conformer B. ^{19}F NMR δ : +15.0 (mult., 3F, $\text{CF}_3\text{N}-\text{OCClMe}$); +11.2 (mult., 3F, $\text{CF}_3\text{N}-\text{OCH}_2$); –26.8 (mult., 2F, CF_2); and –29.1 (mult., 2F, CF_2) ppm for conformer A and +13.0 (dd, 1F, $\text{CF}_3\text{N}-\text{OCClMe}$, $J=22.8$ and 5.8 Hz); +11.2 (mult., 1F, $\text{CF}_3\text{N}-\text{OCH}_2$); –26.8 (mult., 0.67F, CF_2); and –29.1 (mult., 0.67F, CF_2) ppm for conformer B (ratio 3:1). MS m/z : 374/376 (4.0%, M^+); 339 [12.9, ($M-\text{Cl}$) $^+$];

149 (30.2, $C_2F_5NO^+$); 114 (21.8, $C_2F_4N^+$); 91/93 (75.9, $C_2H_2ClNO^+$ and/or $C_3H_4ClO^+$); 75/77 (19.5, C_2ClO^+); 69 (82.5, CF_3^+); 63/65 (25.4, $CClO^+$); and 43 (100.0, $C_2H_3O^+$). In addition, a 1:1 dioxy 1/2-chloropropene copolymer **3n** (nc) (1.04 g, 76.5%) was obtained. [Analysis: Found: C, 22.5; H, 1.2; F, 51.1; N, 7.1%. ($C_7H_5ClF_{10}N_2O_2$)_n requires: C, 22.4; H, 1.3; F, 50.7; N, 7.5%]. IR (ν_{max}) (cm^{-1}): 2959 (w) C–H str.; 1279–1188 (vs) (C–F str.); 1083 (s) (C–O str.); 1047 (s) (N–O str.); and 702 and 714 (m) (CF_3 def.). 1H NMR ($CF_2ClCFCl_2$) δ : 5.06 (br., 2H, CH_2); and 2.65 (s, 3H, CH_3) ppm. ^{19}F NMR δ : +14.4 and +13.5 (2 mult., $2 \times 1.5F$, $CF_3N-OCClMe$); +12.0 (mult., 3F, CF_3N-OCH_2); –18.0 (br., 2F, CF_2); and –24.1 (mult., 2F, CF_2) ppm. MS m/z : 373/375 (4.2%, $C_7H_4ClF_{10}N_2O_2^+$); 339 (1.4, $C_7H_5F_{10}N_2O_2^+$); 150 (10.4, $C_2HF_5NO^+$); 114 (26.8, $C_2F_4N^+$); 92/94 (19.3, $C_3H_5ClO^+$); 91/93 (24.2, $C_3H_4ClO^+$); 69 (81.3, CF_3^+); and 43 (100.0, $C_2H_3O^+$).

(g) With 2-bromopropene – A mixture of **1** (1.19 g, 3.99 mmol) and the alkene (0.68 g, 5.62 mmol) when stored (3 d) gave unchanged alkene (0.19 g, 0.57 mmol, 28% recovered) and 7-bromo-3,3,4,4-tetrafluoro-7-methyl-2,5-bis(trifluoromethyl)-1,6-dioxo-2,5-diazacyclo-octane (**2m**) (nc) (0.43 g, 1.03 mmol, 26%). (Analysis: Found: C, 19.7; H, 1.4; F, 45.6; N, 6.6%; M^+ , 418/420. $C_7H_5BrF_{10}N_2O_2$ requires: C, 20.0; H, 1.2; F, 45.3; N, 6.7%; M , 419), b.p. 162 °C, n_D^{20} 1.3686. IR (ν_{max}) (cm^{-1}): 2950 (w) (C–H str.); 1277–1174 (vs) (C–F str.); 1080 (s) (C–O str.); 1054 and 1021 (N–O str.); and 710 (s) (CF_3 def.). 1H NMR (neat) δ : 5.46 and 5.06 (AB, 2H, CH_AH_B , $J=14.4$ Hz); and 2.74 (s, 3H, CH_3) ppm for conformer A and 5.14 and 4.90 (AB, 1.4H, CH_AH_B , $J=14.5$ Hz); and 2.86 (s, 2.1H, CH_3) ppm for conformer B (ratio 1.4:1.0). ^{19}F NMR δ : +15.8 (mult., 3F, $CF_3N-OCBrMe$); +11.1 (mult., 3F, CF_3N-OCH_2); and –26.8 (mult., 4F, CF_2CF_2) ppm for conformer A and +13.3 (dd, 2.1F, $CF_3N-OCBrMe$, $J=22.6$ and 5.6 Hz); +11.1 (mult., 2.1F, CF_3N-OCH_2); and –26.8 (mult., 2.8F, CF_2CF_2) ppm for conformer B. MS m/z : 418/420 (4.4%, M^+); 339 [26.1, ($M-Br$) $^+$] 149 (16.2, $C_2F_5NO^+$); 135/137 (20.0, $C_3H_4BrO^+$); 114 (15.1, $C_2F_4N^+$); 107/109 (9.7, $CBrO^+$); 69 (56.4, CF_3^+); 43 (100.0, $C_2H_3O^+$); and 29 (13.5, CHO^+). In addition, a 1:1 dioxy 1/2-bromopropene copolymer **3o** (nc) (1.02 g, 61%) was obtained. [Analysis: Found: C, 19.6; H, 1.2; F, 45.2; N, 6.5% ($C_7H_5BrF_{10}N_2O_2$)_n requires: C, 20.0; H, 1.2; F, 45.3; N, 6.6%]. IR (ν_{max}) (cm^{-1}): 3470 (w) (O–H str.); 1269–1186 (vs) (C–F str.); 1092 and 1074 (s) (C–O str.); 1047 (s) (N–O str.); and 714 (m) (CF_3 def.). 1H NMR ($CF_2ClCFCl_2$) δ : 5.17 (br., 2H, CH_2); and 2.84 (s, 3H, CH_3) ppm. ^{19}F NMR δ : +14.9 and +13.4 (2 mult., 3F, $CF_3N-OCBrMe$); +12.0 (mult., 3F, CF_3N-OCH_2); –17.4 (br., 2F, CF_2); and –24.0

(mult., 2F, CF_2) ppm. MS m/z : 757/759 (1.4%, $C_{14}H_{10}BrF_{20}N_4O_4^+$); 339 (3.9, $C_6H_5F_{10}N_2O_2^+$); 150 (8.5, $C_2HF_5NO^+$); 114 (18.6, $C_2F_4N^+$); 69 (73.5, CF_3^+); 43 (100.0, $C_2H_3O^+$); and 29 (11.6, CHO^+).

(h) With (*E*)-1,2-dichloroethene – A mixture of **1** (1.25 g, 4.19 mmol) and the *trans*-alkene (0.50 g, 5.15 mmol) when stored (70 d) gave unchanged alkene (0.09 g, 0.93 mmol, 18% recovered), perfluoro-2-azapropene (0.02 g, 0.18 mmol, 4.5%) and the 1:1 adduct **2n** (0.45 g, 1.14 mmol, 27%). (Analysis: Found: C, 18.3; H, 0.6; F, 48.2; N, 6.9%; M^+ , 394/396/398. Calc. for $C_6H_2Cl_2F_{10}N_2O_2$: C, 18.2; H, 0.5; F, 48.1; N, 7.1%; M , 395), b.p. 155 °C, n_D^{20} 1.3559. In addition, a 1:1 dioxy 1/1,2-dichloroethene copolymer **3e** (1.14 g, 69%) was obtained. [Analysis: Found: C, 18.3; H, 0.6; F, 47.8; N, 7.1%. Calc. for ($C_6H_2Cl_2F_{10}N_2O_2$)_n: C, 18.2; H, 0.5; F, 48.1; N, 7.1%].

(i) With (*Z*)-1,2-dichloroethene – A mixture of **1** (1.23 g, 4.13 mmol) and the *cis*-alkene (0.53 g, 5.49 mmol) when stored (70 d) gave the unchanged alkene (0.30 g, 3.09 mmol, 56.5% recovered), perfluoro-2-azapropene (0.03 g, 0.29 mmol, 12.5%), unchanged **1** (0.53 g, 1.78 mmol, 43% recovered) and 7,8-dichloro-3,3,4,4-tetrafluoro-2,5-bis(trifluoromethyl)-1,6-dioxo-2,5-diazacyclo-octane (**2n**) (nc) (0.33 g, 0.84 mmol, 36%). (Analysis: Found: C, 18.2; H, 0.7; F, 48.1; N, 6.9%; M^+ , 394/396/398. $C_6H_2Cl_2F_{10}N_2O_2$ requires: C, 18.2; H, 0.5; F, 48.1; N, 7.1%; M , 395), b.p. 155 °C, n_D^{20} 1.3560. IR (ν_{max}) (cm^{-1}): 1276–1193 (vs) (C–F str.); 1085 (m) (C–O str.); 1040 (s) (N–O str.); 968 (w) (C–N str.); and 707 (s) (CF_3 def.). 1H NMR (neat) δ : 6.29 (s, $CHClCHCl$) ppm. ^{19}F NMR δ : +11.0 (d mult., 6F, $2CF_3N$, $J=23.0$ Hz); –28.3 and –39.0 (d and d mult., 4F, $CF_A F_A-CF_B F_B$, $J_{AA'}=201$, $J_{BB'}=205$ Hz) ppm. MS m/z : 394/396/398 (2.3%, M^+); 375/377/379 [2.4, ($M-F$) $^+$]; 359/361 [2.6, ($M-Cl$) $^+$]; 282 (12.0, $C_4F_{10}N_2O^+$); 149 (64.8, $C_2F_5NO^+$); 114 (31.1, $C_2F_4N^+$); 111/113/115 (16.1, $C_2HCl_2O^+$); 69 (100.0, CF_3^+); and 49/51 (16.0, CH_2Cl^+). In addition, a 1:1 dioxy 1/1,2-dichloroethene copolymer **3e** (0.52 g, 56%) was obtained. [Analysis: Found: C, 18.5; H, 0.7; F, 48.0; N, 7.0%. Calc. for ($C_6H_2Cl_2F_{10}N_2O_2$)_n: C, 18.2; H, 0.5; F, 48.1; N, 7.1%].

(j) With trichloroethene – A mixture of **1** (1.26 g, 4.23 mmol) and the alkene (1.57 g, 11.94 mmol) when stored (10 d) gave the unchanged alkene (1.04 g, 7.91 mmol, 66% recovered) and 3,3,4,4-tetrafluoro-7,7,8-trichloro-2,5-bis(trifluoromethyl)-1,6-dioxo-2,5-diazacyclo-octane (**2o**) (nc) (0.49 g, 1.14 mmol, 27%). (Analysis: Found: C, 16.9; H, 0.4; Cl, 24.9; F, 44.3; N, 6.4%. $C_6HCl_3F_{10}N_2O_2$ requires: C, 16.8; H, 0.2; Cl, 24.8; F, 44.2; N, 6.5%), b.p. 175 °C, n_D^{20} 1.3731. IR

(ν_{\max}) (cm^{-1}): 2994 (vw) (C–H str.); 1276–1179 (s) (C–F str.); 1084 (s) (C–O str.); 1043 (s) (N–O str.); 957 (m) (C–N str.); and 709 (m) (CF_3 def.). ^{19}F NMR (neat) δ : +14.0 (dd, 3F, $\text{CF}_3\text{NOCCl}_2$, $J=24.0$ and 3.9 Hz); +11.8 (dd, 3F, $\text{CF}_3\text{N–OCHCl}$, $J=22.4$ and 4.4 Hz); –25.5 and –29.0 (AB mult., 2F, CF_AF_B , $J_{A-B}=215$ Hz); and –36.0 and –39.5 (mult., 2F, CF_2) ppm. MS m/z : 409/411 [0.4%, (M–F) $^+$], 393/395/397 [3.5, (M–Cl) $^+$]; 199 (10.9, $\text{C}_3\text{F}_7\text{NO}^+$); 149 (28.0, $\text{C}_2\text{F}_5\text{NO}^+$); 114 (21.5, $\text{C}_2\text{F}_4\text{N}^+$); 69 (100.0, CF_3^+); and 63/65 (18.6, CClO^+). In addition, a 1:1 dioxyl 1/trichloroethene copolymer **3d** (1.27 g, 70%) was obtained. [Analysis: Found: C, 17.1; H, 0.5; Cl, 24.4; F, 44.4; N, 6.3%. Calc. for $(\text{C}_6\text{HCl}_3\text{F}_{10}\text{N}_2\text{O}_2)_n$: C, 16.8; H, 0.2; Cl, 24.8; F, 44.2; N, 6.5%.]

(k) With chlorotrifluoroethene – A mixture of **1** (1.14 g, 3.83 mmol) and the fluoroalkene (0.68 g, 5.85 mmol) when stored (3 d) gave the unchanged alkene (0.26 g, 2.33 mmol, 38% recovered) and 7-chloro-3,3,4,4,7,8,8-heptafluoro-2,5-bis(trifluoromethyl)-1,6-dioxo-2,5-diazacyclo-octane (**2p**) (nc) (0.98 g, 2.36 mmol, 61.5%). (Analysis: Found: C, 17.6; F, 59.5; N, 6.6%; M $^+$, 414/416. $\text{C}_6\text{ClF}_{13}\text{N}_2\text{O}_2$ requires: C, 17.4; F, 59.6; N, 6.8%; M, 414.5), b.p. 136°C , n_D^{20} 1.3142. IR (ν_{\max}) (cm^{-1}): 1286–1139 (vs) (C–F str.); 1090 (s) (C–O str.); 1056 and 1041 (s) (N–O str.); and (s) (CF_3 def.). ^{19}F NMR (neat) δ : +12.0 (ddd, 3F, $\text{CF}_3\text{N–OCF}_2$, $J=23.5$, 11.4 and 4.0 Hz); +11.7 (ddd, 3F, $\text{CF}_3\text{N–OCFCl}$, $J=22.3$, 9.3 and 4.8 Hz); –12.0 and –12.9 (dd and mult., $\text{CF}_2\text{–O}$, $J=13.1$ and 3.4 Hz); –17.2 (mult., 1F, CFCl–O); –26.7 and –30.2 (2d mult., 2F, $\text{CF}_2\text{–N}$, $J=113$ Hz); and –36.2 and –40.0 (2 mult., 2F, $\text{CF}_2\text{–N}$) ppm. MS m/z : 414/416 (0.1%, M $^+$); 395.397 [2.1, (M–F) $^+$]; 379 [9.5, (M–Cl) $^+$]; 199 (32.1, $\text{C}_3\text{F}_7\text{NO}^+$); 196/198 (16.9, $\text{C}_3\text{ClF}_5\text{NO}^+$); 149 (19.0, $\text{C}_2\text{F}_5\text{NO}^+$); 116/118 (6.5, C_2ClF_3^+); 114 (15.1, $\text{C}_2\text{F}_4\text{N}^+$); 100 (25.9, C_2F_4^+); 99 (10.7, CF_3NO^+); and 69 (100.0, CF_3^+). In addition, a 1:1 dioxyl 1/chlorotrifluoroethene copolymer **3p** (nc) (0.49 g, 31%) was obtained. [Analysis: Found: C, 17.1; Cl, 8.6; F, 59.4; N, 6.6%. ($\text{C}_6\text{ClF}_{12}\text{N}_2\text{O}_2$) $_n$ requires: C, 17.4; Cl, 8.6; F, 59.6; N, 6.8%.] IR (ν_{\max}) (cm^{-1}): 1281–1156 (vs) (C–F str.); 1111 (s) (C–O str.); 1049 (s) (N–O str.); and 735 (s) (CF_3 def.). ^{19}F NMR ($\text{CF}_2\text{ClCFCl}_2$) δ : +12.5 (mult., 6F, $2\text{CF}_3\text{N}$); +3.8 (s, 1F, CFCl); –11.7 (s, 2F, $\text{CF}_2\text{–O}$); and –20.0 (mult., 4F, CF_2CF_2) ppm. MS m/z : 828/830/832 (2.3%, $\text{C}_{12}\text{Cl}_2\text{F}_{26}\text{N}_4\text{O}_4^+$); 809/811/813 (1.8, $\text{C}_{12}\text{Cl}_2\text{F}_{25}\text{N}_4\text{O}_4^+$); 793/795 (1.9, $\text{C}_{12}\text{ClF}_{26}\text{N}_4\text{O}_4^+$); 379 (3.2, $\text{C}_6\text{F}_{13}\text{N}_2\text{O}_2^+$); 246/248 (10.1, $\text{C}_4\text{ClF}_7\text{NO}^+$); 199 (6.6, $\text{C}_3\text{F}_7\text{NO}^+$); 196/198 (3.9, $\text{C}_3\text{ClF}_5\text{NO}^+$); 164 (10.1, $\text{C}_3\text{F}_6\text{N}^+$); 149 (14.9, $\text{C}_2\text{F}_5\text{NO}^+$); 130 (8.9, $\text{C}_2\text{F}_4\text{NO}^+$); 114 (29.9, $\text{C}_2\text{F}_4\text{N}^+$); 69 (100.0, CF_3^+); and 47 (16.4, CFO^+).

(l) With bromotrifluoroethene – A mixture of **1** (1.26 g, 4.23 mmol) and the alkene (0.97 g, 6.02 mmol) when stored (2 d) gave the unchanged alkene (0.30 g, 1.86 mmol, 31%) and 7-bromo-3,3,4,4,7,8,8-heptafluoro-2,5-bis(trifluoromethyl)-1,6-dioxo-2,5-diazacyclo-octane (**2q**) (nc) (1.51 g, 3.29 mmol, 78%). (Analysis: Found: C, 16.0; F, 53.3; N, 6.1%; $\text{C}_6\text{BrF}_{13}\text{N}_2\text{O}_2$ requires: C, 16.0; F, 53.8; N, 6.1%), b.p. 151°C , n_D^{20} 1.3270. IR (ν_{\max}) (cm^{-1}): 1285–1135 (vs) (C–F str.); 1091 (s) (C–O str.); 1071 and 1056 (s) (N–O str.); and 711 (s) (CF_3 def.). ^{19}F NMR (neat) δ : +12.0 (ddd, 3F, $\text{CF}_3\text{N–OCF}_2$, $J=24.0$, 11.8 and 3.9 Hz); +11.8 (ddd, 3F, $\text{CF}_3\text{N–OCFBr}$, $J=22.8$, 8.0 and 2.0 Hz); –10.1 and –10.3 (2 mult., 2F, $\text{CF}_2\text{–O}$); –15.5 (mult., 1F, CFBr–O); –26.8 and –30.3 (2d mult., 2F, $\text{CF}_2\text{–N}$, $J=125$ Hz); and –36.4 and –40.2 (2 mult., 2F, $\text{CF}_2\text{–N}$) ppm. MS m/z : 379 [6.1%, (M–Br) $^+$]; 199 (5.7, $\text{C}_3\text{F}_7\text{NO}^+$); 164 (7.2, $\text{C}_3\text{F}_6\text{N}^+$); 149 (20.5, $\text{C}_2\text{F}_5\text{NO}^+$); 114 (23.2, $\text{C}_2\text{F}_4\text{N}^+$); 100 (8.5, C_2F_4^+); 97 (6.3, $\text{C}_2\text{F}_3\text{O}^+$); 69 (100.0, CF_3^+); and 47 (11.7, CFO^+). In addition, a 1:1 dioxyl 1/bromotrifluoroethene copolymer **3q** (nc) (0.36 g, 18.5%) was obtained. [Analysis: Found: C, 16.0; N, 6.2%. ($\text{C}_6\text{BrF}_{13}\text{N}_2\text{O}_2$) $_n$ requires: C, 15.7; N, 6.1%.] IR (ν_{\max}) (cm^{-1}): 1276–1160 (vs) (C–F str.); 1095 (s) (C–O str.); 1057 (s) (N–O str.); and 715 (m) (CF_3 def.). ^{19}F NMR ($\text{CF}_2\text{ClCFCl}_2$) δ : +13.3 (mult., 6F, $2\text{CF}_3\text{N}$); +4.1 (s, 1F, CFBr); –10.0 (s, 2F, $\text{CF}_2\text{–O}$); and –20.0 (mult., 4F, CF_2CF_2) ppm. MS m/z : 423/425 (1.1%, $\text{C}_6\text{BrF}_{12}\text{N}_2\text{O}^+$); 246 (7.4, $\text{C}_4\text{F}_8\text{NO}_2^+$); 164 (10.6, $\text{C}_3\text{F}_6\text{N}^+$); 149 (6.6, $\text{C}_2\text{F}_5\text{NO}^+$); 130 (9.9, $\text{C}_2\text{F}_4\text{NO}^+$); 114 (29.2, $\text{C}_2\text{F}_4\text{N}^+$); 97 (9.8, $\text{C}_2\text{F}_3\text{O}^+$); 69 (100.0, CF_3^+); and 47 (17.5, CFO^+).

(m) With 1,1-dichlorodifluoroethene – A mixture of **1** (1.34 g, 4.50 mmol) and the fluoroalkene (0.83 g, 6.24 mmol) when stored (5 d) gave the unchanged alkene (0.225 g, 1.69 mmol, 27% recovered) and 7,7-dichloro-3,3,4,4,8,8-hexafluoro-2,5-bis(trifluoromethyl)-1,6-dioxo-2,5-diazacyclo-octane (**2r**) (nc) (1.11 g, 2.58 mmol, 57.5%). (Analysis: Found: C, 16.9; Cl, 16.7; F, 52.7; N, 6.3%. $\text{C}_6\text{Cl}_2\text{F}_{12}\text{N}_2\text{O}_2$ requires: C, 16.7; Cl, 16.5; F, 52.9; N, 6.5%), b.p. 144°C , n_D^{20} 1.3400. IR (ν_{\max}) (cm^{-1}): 1284–1165 (vs) (C–F str.); 1085 (s) (C–O str.); 1058 and 1030 (s) (N–O str.); and 709 (s) (CF_3 def.). ^{19}F NMR (neat) δ : +13.7 (dd, 3F, $\text{CF}_3\text{N–OCCl}_2$, $J=23.8$ and 4.1 Hz); +12.0 (ddd, 3F, $\text{CF}_2\text{N–OCF}_2$, $J=23.8$, 8.6 and 3.6 Hz); –4.3 and –15.9 (dd and d mult., 2F, $\text{CF}_A\text{F}_A\text{–CCl}_2$, $J=142$ and 3.2 Hz; $J=142$ Hz); –24.7 and –28.6 (2 \times d mult., 2F, $\text{CF}_B\text{F}_B\text{–N}$, $J=138$ Hz); and –35.2 and –39.0 (2 mult., $\text{CF}_2\text{–N}$) ppm. MS m/z : 411/413/415 [1.5%, (M–F) $^+$]; 395/397 [9.4, (M–Cl) $^+$]; 199 (17.9, $\text{C}_3\text{F}_7\text{NO}^+$); 149 (44.1, $\text{C}_2\text{F}_5\text{NO}^+$); 132/134/136 (16.3, $\text{C}_2\text{Cl}_2\text{F}_2^+$); 100 (16.9, C_2F_4^+); 85 (19.7, C_3FNO^+); 69 (100.0, CF_3^+); and 63/65 (29.9, CClO^+). In addition, a 1:1 dioxyl 1/1,1-dichlorodi-

fluoroethene copolymer **3r** (nc) (0.65 g, 33.5%) was obtained. [Analysis: Found: C, 17.1; Cl, 16.4; F, 52.5; N, 6.2%. ($C_6Cl_2F_{12}N_2O_2$)_n requires: C, 16.7; Cl, 16.5; F, 52.9; N, 6.5%.] IR (ν_{max}) (cm^{-1}): 1288–1189 (vs) (C–F str.); 1026 (s) (N–O str.); and 708 (m) (CF_3 def.). ^{19}F NMR ($CF_2ClCFCl_2$) δ : +14.2 (mult., 3F, $CF_3N-OCCL_2$); +12.9 (mult., 3F, CF_3N-OCF_2); –9.3 (s, 2F, CF_2CCl_2); –17.5 (br., 2F, CF_2-N); and –20.0 (mult., 2F, CF_2-N) ppm. MS m/z : 395/397 ($C_6ClF_{12}N_2O_2^+$); 316/318/320 (14.8, $C_4Cl_2F_8N_2O_2^+$); 199 (11.4, $C_3F_7NO^+$); 168/170 (25.0, $C_2ClF_5N^+$); 149 (38.5, $C_2F_5NO^+$); 132/134 (15.3, $C_2Cl_2F_2^+$); 114 (26.3, $C_2F_4N^+$); 85/87 (25.2, $CClF_2^+$); 82/84/86 (13.4, CCl_2^+); 60 (100.0, CF_3^+); and 63/65 (49.5, $CClO^+$).

Hydrolysis of the 1:1 dioxyl 1/acryloyl chloride copolymer **3f**

A mixture of copolymer **3f** (0.97 g), water (5 cm^3) and 1,1,2-trichlorotrifluoroethane (5 cm^3) was sealed *in vacuo* in a Rotaflo tube (c. 100 cm^3) and the tube shaken at room temperature (48 h). This gave (after removal of the volatile material) a 1:1 dioxyl **1**/acrylic acid copolymer **3j** (nc) (0.83 g, 89.5%). [Analysis: Found: C, 22.7; H, 1.3; F, 51.7%. ($C_7H_4F_{10}N_2O_4$)_n requires: C, 22.7; H, 1.1; F, 51.3%.] IR (ν_{max}) (cm^{-1}): 3509 (m) and 3215 (s) (O–H str.); 1739 and 1692 (s) (C=O str.); 1284–1149 (vs) (C–F str.); 1046 (s) (N–O str.); and 708 (s) (CF_3 def.). 1H NMR (Me_2CO) δ : 9.20 (br., 1H, CO_2H); 5.54 (br., 1H, CH–O); and 4.26 (br., 2H, CH_2-O) ppm. ^{19}F NMR δ : +12.6 (mult., 3F, $CF_3N-OCHCO_2H$); +12.0 (mult., 3F, CF_3N-OCH_2); and –21.6 and –24.5 (br., 4F, CF_2CF_2) ppm.

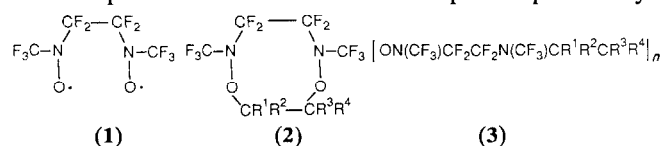
Hydrolysis of the dioxyl **1**/acryloyl fluoride 1:1 adduct **2j**

A mixture of the 1:1 adduct **2j** (0.19 g, 0.51 mmol) and water (5 cm^3) when sealed *in vacuo* in a Rotaflo tube (c. 100 cm^3) and the tube shaken at room temperature for 5 min gave (after removal of the volatile material) 3,3,4,4-tetrafluoro-2,5-bis(trifluoromethyl)-1,6-dioxia-2,5-diazacyclo-octane carboxylic acid (**2s**) (nc). (Analysis: Found: C, 22.8; H, 1.2; F, 51.0%; M^+ , 370. $C_7H_4F_{10}N_2O_4$ requires: C, 22.7; H, 1.1; F, 51.3%, M , 370), m.p. 98.5 °C. IR (ν_{max}) (cm^{-1}): 1754 (s) (C=O str.); 1295–1166 (vs) (C–F str.); 1089 and 1076 (s) (C–O str.); 1053 and 1047 (s) (N–O str.); and 709 (s) (CF_3 def.). 1H NMR (Me_2CO) δ : 9.35 (br., 1H, CO_2H); 4.75 (br., 1H, CH–O); and 4.17 (br., 1H, CH_2-O) ppm. ^{19}F NMR δ : +11.8 (mult., 6F, $2CF_3N$); –26.1 and –29.4 (2 mult., 2F, CF_2-N); and –37.8 (mult., 2F, CF_2-N) ppm. MS m/z 370 (0.5%, M^+); 149 (18.1, $C_2F_5NO^+$); 134 (17.8, $C_2HF_5N^+$); 114 (38.9, $C_2F_4N^+$); 95 (8.3, $C_2F_3N^+$); 92 (38.5, $C_2F_2NO^+$); 69 (100.0, CF_3^+); and 44 (62.5, CO_2^+).

Results and discussion

From previous results [2, 7], it was clear that the formation of the cyclic 1:1 adducts **2** from the reaction of dioxyl **1** with alkenes would require a gas-phase reaction. Furthermore, since the nitroxide $(CF_3)_2NO\cdot$ will not only add to alkenes but also abstract allylic hydrogen atoms, it was probable that the dioxyl **1** would react analogously. Dioxyl **1** could also abstract hydrogen atoms from methylene or methine groups present in the initial products. This could lead to complex mixtures which might be difficult to separate on the small (c. 4 mmol of **1**) reaction scale envisaged. Also, if the reaction with an alkene in the liquid phase was slow, it would be considerably slower in the gas phase because of the lower reactant concentration.

In order to determine which hydrogen-containing alkenes were suitable to be investigated for gas-phase reactions, the liquid-phase reactions of a variety of such alkenes were studied initially and the results obtained are compared in Table 1 with those reported previously.



(1)	(2)	(3)
(2)	(3)	
a; $R^1 = H, R^2 = R^3 = R^4 = F$	a; $R^1 = H, R^2 = R^3 = R^4 = F$	
b; $R^1 = R^2 = R^3 = H, R^4 = F$	b; $R^1 = R^2 = R^3 = H, R^4 = F$	
c; $R^1 = R^2 = H, R^3 = R^4 = F$	c; $R^1 = R^2 = H, R^3 = R^4 = F$	
d; $R^1 = R^2 = R^3 = R^4 = H$	d; $R^1 = H, R^2 = R^3 = R^4 = Cl$	
e; $R^1 = R^2 = R^3 = R^4 = F$	e; $R^1 = R^2 = H, R^3 = R^4 = Cl$	
f; $R^1 = R^2 = R^3 = F, R^4 = CF_3$	f; $R^1 = R^2 = R^3 = H, R^4 = COCl$	
g; $R^1 = R^2 = H, R^3 = R^4 = Cl$	g; $R^1 = R^2 = R^3 = R^4 = H$	
h; $R^1 = R^2 = R^3 = H, R^4 = Cl$	h; $R^1 = R^2 = R^3 = R^4 = F$	
i; $R^1 = R^2 = R^3 = H, R^4 = Br$	i; $R^1 = R^2 = R^3 = H, R^4 = CF_3$	
j; $R^1 = R^2 = R^3 = H, R^4 = COF$	j; $R^1 = R^2 = R^3 = H, R^4 = CO_2H$	
k; $R^1 = R^2 = R^3 = H, R^4 = COCl$	k; $R^1 = R^2 = H, R^3 = R^4 = Cl$	
l; $R^1 = R^2 = H, R^3 = Cl, R^4 = Me$	l; $R^1 = R^2 = R^3 = H, R^4 = Cl$	
m; $R^1 = R^2 = H, R^3 = Br, R^4 = Me$	m; $R^1 = R^2 = R^3 = H, R^4 = Br$	
n; $R^1 = R^2 = H, R^3 = R^4 = Cl$	n; $R^1 = R^2 = H, R^3 = Cl, R^4 = Me$	
o; $R^1 = H, R^2 = R^3 = R^4 = Cl$	o; $R^1 = R^2 = H, R^3 = Br, R^4 = Me$	
p; $R^1 = R^2 = R^3 = F, R^4 = Cl$	p; $R^1 = R^2 = R^3 = F, R^4 = Cl$	
q; $R^1 = R^2 = R^3 = F, R^4 = Br$	q; $R^1 = R^2 = R^3 = F, R^4 = Br$	
r; $R^1 = R^2 = F, R^3 = R^4 = Cl$	r; $R^1 = R^2 = F, R^3 = R^4 = Cl$	
s; $R^1 = R^2 = R^3 = H, R^4 = CO_2H$	s; $R^1 = R^2 = R^3 = H, R^4 = COF$	

The IR spectra of the 1:1 copolymers **3a–3f** afforded no evidence that hydrogen abstraction had occurred. However, although the ethene product analysed correctly for the 1:1 copolymer **3g**, it showed IR absorptions at 3390 and 3280 [(w) (O–H str.)] and 1835 [(w) (C=O str.)] cm^{-1} indicating that hydrogen abstraction had taken place to a limited degree; the copolymer has been made previously [7].

The polymers formed from the reaction involving 2-methylpropene (at 20 °C and –78 °C) and but-1-ene gave low C and H elemental analysis figures for a 1:1 copolymer, showing that the products contained a higher proportion of dioxyl **1** units than alkene units. That

TABLE 1. Liquid-phase reaction of dioyl **1** with alkenes

Alkene	Molar ratio alkene/ 1	Conditions		Recovered alkene (%)	Products (%)			
		Temp. (°C)	Time (d)		Polymer	1:1 adduct		
CHF=CF ₂	1.6	20	0.67	36	3a	90	2a	trace
CH ₂ =CHF	1.14	20	11	28	3b	95	2b	4
CH ₂ =CF ₂	1.36	20	21	26	3c	91	2c	3
CHCl=CCl ₂	2.1	20	0.5	52	3d	96		
(Z)-CHCl=CHCl	1.74	20	2	42.5	3e	99		
CH ₂ =CHCOCl	2	20	0.5	52	3f	98		
CH ₂ =CH ₂	1.4	20	5	28.5	3g	91	2d	trace
CH ₂ =CMe ₂	1.2	20	0.07	19		97 ^e		
CH ₂ =CMe ₂	1.5	-78	1	22		93 ^e		
CH ₂ =CHEt	1.4	20	0.42	65		93 ^e		
CH ₂ =CHCO ₂ H	1.14	20	21			95 ^e		
(Z)-HO ₂ CCH=CHCO ₂ H	0.91 ^c	52	1.3			55 ^e		
CF ₂ =CF ₂	1.0	20	0.75	0	3h	93	2e	3
CF ₂ =CFCF ₃ ^a	1.1	20	6	8.5	3i	86	2f	7
CH ₂ =CF ₂ ^b		20	4 ^d		3c	73	2c	5

^aRef. 2.^bRef. 8.^cIn CF₂ClCFCl₂ solvent.^dReaction incomplete.^eNot a 1:1 copolymer.

hydrogen abstraction had occurred was confirmed by IR bands in the range 3560–3330 [(m) (O–H str.)] and 1815–1770 (C=O str.) cm⁻¹; the but-1-ene polymer also showed an IR band at 1669 [(m) (C=C str.)] cm⁻¹.

The mixture of **1** and acrylic acid formed a white solid when the reaction tube was warmed up from -196 °C to room temperature, but the purple colour of the dioyl **1** slowly faded over a period of 3 weeks. It seems probable that dioyl **1** initiated homopolymerisation of the alkene to a considerable extent in the initial stages of the reaction and then slowly attacked the polymer backbone via hydrogen abstraction. However, hydrolysis with water of a solution of the acryloyl chloride 1:1 copolymer **3f** in CF₂ClCFCl₂ solvent afforded the acrylic acid 1:1 copolymer **3y** in high yield (89.5%).

To dissolve the alkene, the reaction between maleic acid and **1** was carried out in CF₂ClCFCl₂ solvent but the product formed did not analyse correctly for a 1:1 copolymer.

The results obtained from these liquid-phase reactions illustrate clearly the limitations which need to be imposed on the gas-phase reactions. Such reactions must be restricted to simple ethenes or halogenated propenes due to the possibility of hydrogen abstraction occurring, i.e. alkenes such as CH₂=CMe₂ and CH₂=CHEt are not suitable. Also for a gas-phase reaction to be complete in a reasonable time at room temperature (up to 6 weeks) the corresponding liquid-phase reaction needed to have reached completion in a relatively short period of time

(2 d or less), i.e. alkenes such as CH₂=CH₂, CH₂=CHF, CH₂=CF₂ and CH₂=CHCO₂H were not suitable.

Firstly, the gas-phase reaction between dioyl **1** and an excess of the alkene CH₂=CCl₂ was studied over a range of pressures and reactant ratios. This alkene was chosen because it has a relatively low boiling point (39 °C). Hence it can be handled easily in a vacuum system and the excess of alkene should be capable of ready separation from the cyclic 1:1 adduct **2**. Also, since the alkene CHCl=CCl₂ was very reactive in the liquid-phase reaction with **1**, it was expected that the gas-phase reaction involving CH₂=CCl₂ would be complete in a relatively short period of time at room temperature. The results obtained are summarised in Table 2.

All the reactions were completed in a short period of time (≤6 d) and the results show that the yield of the heterocycle **2g** is (i) independent of alkene concentration [yield of **2g** constant (50±1%) when the dioyl **1** concentration kept constant (±4%, experiments 2–5) and the concentration of alkene varied (15–98% excess] and (ii) dependent upon large variations in the dioyl **1** concentration [the lowest concentration of **1** (experiment 6) gave the highest yield of **2g** (56%), whilst a higher concentration of **1** (experiment 1) gave the lowest yield of **2g** (34.5%)].

The reaction involves the formation of the intermediate diradical **4** and the higher the dioyl **1** concentration the more effectively is **4** scavenged by **1** to give a new dioyl **5** before it can cyclise to the 1:1

TABLE 2. Reaction of dioxyl 1 with the alkene $\text{CH}_2=\text{CCl}_2$ in the gas phase (10 dm³ bulb)

Expt. No.	Dioxyl 1 (mmol)	Alkene (mmol)	Excess of alkene (%)	Molar ratio alkene/1	Pressure (atm)	Alkene recovered (%)	Products (%)	
							3k	2g
1	3.76 ^a (7.52)	5.78 ^a (11.52)	53.5	1.54	0.046	41	61.5	34.5
2	4.40	5.05	14.5	1.15	0.023	15	43.5	50
3	4.33	6.29	45.5	1.45	0.026	31	45.5	49.5
4	4.19	6.70	60.0	1.60	0.026	34.5	46	51
5	4.53	8.97	98.0	1.98	0.032	45.5	46.5	49
6	2.45	3.50	43.0	1.43	0.014	35.5	43.5	56

^aCarried out in a 5 dm³ bulb; equivalent quantities for a 10 dm³ bulb are given in parentheses.

TABLE 3. Gas-phase reaction of dioxyl 1 with alkenes at room temperature

Alkene	Molar ratio alkene/1	Pressure (atm)	Time (d)	Recovered alkene (%)	Products (%)			
					Polymer		Heterocycle	
* $\text{CH}_2=\text{CHCl}$	1.42	0.026	56	36.5	3l	61.5	2h	31.5
* $\text{CH}_2=\text{CHBr}$	1.53	0.024	35	36	3m	53.5	2i	42.5
* $\text{CH}_2=\text{CHCOF}$	1.42	0.029	42	29		c. 77	2j	16
* $\text{CH}_2=\text{CHCOCl}$	1.12	0.026	21	c. 15	3f	75	2k	11.5
* $\text{CH}_2=\text{CClMe}$	1.57	0.022	3	34.5	3n	76.5	2l ^c	23.5
* $\text{CH}_2=\text{CBrMe}$	1.41	0.023	3	28	3o	61	2m ^d	26
* $\text{CH}_2=\text{CCl}_2$	1.45	0.026	4	31	3k	45.5	2g	49.5
(<i>E</i>)- $\text{CHCl}=\text{CHCl}$	1.23	0.023	70	18	3e	69	2n	27
(<i>Z</i>)- $\text{CHCl}=\text{CHCl}$	1.33	0.023	70 ^a	56.5	3e	56	2n	36
* $\text{CHCl}=\text{CCl}_2$	2.82	0.039	10	66	3d	70	2o	27
* $\text{CF}_2=\text{CFCl}$	1.52	0.023	3	38	3p	31	2p	61.5
* $\text{CF}_2=\text{CFBr}$	1.42	0.025	2	31	3q	18.5	2q	78
* $\text{CF}_2=\text{CCl}_2$	1.39	0.026	5	27	3r	33.5	2r	57.5
$\text{CF}_2=\text{CF}_2$		0.07	1		3h	48	2e	52 ^c
$\text{CF}_2=\text{CFCF}_3$	6.0	0.02	7 ^a	93 ^b			2f	63 ^f

*Expected site of radical attack.

^aReaction incomplete.

^bUnchanged dioxyl 1 (62% recovered) also present.

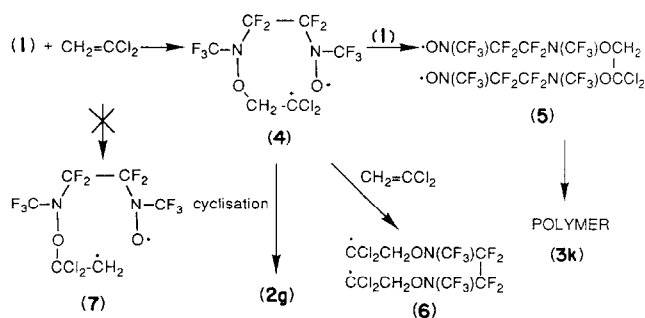
^cTwo conformers; ratio 3:1.

^dTwo conformers; ratio 1.4:1.

^eRef. 7.

^fRef. 2.

adduct 2g. Since the yield of 2g is independent of the alkene concentration, the reaction of diradical 4 with alkene to give the diradical 6 is less favoured (Scheme 1).



Scheme 1.

Attack by dioxyl 1 on the alkene would be expected to occur exclusively at the CH_2 carbon to give 4 which is stabilised by the two chlorine atoms; attack at the CCl_2 carbon would give a non-stabilised primary radical 7.

The reaction of dioxyl 1 with various halogeno-ethenes and -propenes were then studied and the results obtained are shown in Table 3.

From Table 3, the relative reactivities of the hydrogen- and fluorine-containing alkenes towards dioxyl 1 are $\text{CH}_2=\text{CBrMe} \sim \text{CH}_2=\text{CClMe} > \text{CH}_2=\text{CCl}_2 > \text{CHCl}=\text{CCl}_2 > \text{CH}_2\text{CHCOCl} > \text{CH}_2=\text{CHBr} > \text{CH}_2=\text{CHCOF} > \text{CH}_2=\text{CHCl} > (E) = \text{CHCl}=\text{CHCl} > (Z) = \text{CHCl}=\text{CHCl}$ and $\text{CF}_2=\text{CF}_2 > \text{CF}_2=\text{CFBr} > \text{CF}_2=\text{CFCl} > \text{CF}_2=\text{CCl}_2 > \text{CF}_2=\text{CFCF}_3$, while the

yields of the 1:1 adduct, heterocycle **2**, are in the order $\text{CH}_2=\text{CCl}_2 > \text{CH}_2=\text{CHBr} > (\text{Z})\text{-CHCl}=\text{CHCl} > \text{CH}_2=\text{CHCl} > \text{CHCl}=\text{CCl}_2 \sim (\text{E})\text{-CHCl}=\text{CHCl} > \text{CH}_2=\text{CBrMe} > \text{CH}_2=\text{CClMe} > \text{CH}_2=\text{CHCOF} > \text{CH}_2=\text{CHCOCl}$ and $\text{CF}_2=\text{CFBr} > \text{CF}_2=\text{CFCF}_3 > \text{CF}_2=\text{CFCl} > \text{CF}_2=\text{CCl}_2 > \text{CF}_2=\text{CF}_2$.

The most electron-rich hydrogen-containing alkenes were observed to be the most reactive, i.e. the 2-halogenopropenes, as expected for reaction with an electrophilic radical and the general order of reactivity of the remaining alkenes was that expected on the basis of the order of intermediate radical stability, i.e. $-\dot{\text{C}}\text{Cl}_2 > -\dot{\text{C}}\text{HCOX} \sim -\dot{\text{C}}\text{HBr} > -\dot{\text{C}}\text{HCl}$. However, the order of reactivity observed for the fluoroalkenes was not that expected on the basis of intermediate radical stability ($-\dot{\text{C}}\text{FBr} \sim -\dot{\text{C}}\text{Cl}_2 > -\dot{\text{C}}\text{FCl} > -\dot{\text{C}}\text{FCF}_3 > -\dot{\text{C}}\text{F}_2$).

The products are formed via coupling between the carbon-centred radical terminus in the intermediate diradical **4** and an oxyl radical, with intramolecular reaction giving 1:1 adduct **2** and intermolecular reaction leading eventually to copolymer **3**. A number of factors (entropy, steric interactions, etc.) would be involved in determining which reaction is the more favourable in a particular case, and it is not possible on the limited evidence available to explain the observed variations in the yields of the 1:1 adducts **2**.

Only with the copolymer **3o** formed from 2-bromopropene was any evidence obtained for hydrogen abstraction having taken place in any of these reactions. The IR spectrum of copolymer **3o** contained a weak bond at 3470 cm^{-1} assigned to O-H stretch, but the material analysed correctly for a 1:1 copolymer.

The copolymer obtained from the acryloyl fluoride reaction did not analyse correctly for the 1:1 copolymer **3s** and the 1:1 adduct **2j** formed in this reaction on storage changed from a liquid to a white solid. This was attributed to partial hydrolysis, and hydrolysis of the compound **2j** with an excess of water afforded the corresponding carboxylic acid **2s** in good yield (84.5%).

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