The reactions of bis(trifluoromethyl)amino-oxyl and perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) with 3,3,3-trichloropropene and 3,3,3-trichloro-2-methylpropene

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Abstract

Reaction of the oxyl $(CF_3)_2NO\cdot$ (**1**) with 3,3,3-trichloropropene (**2**) at *c.* 20 °C afforded the 2:1 adduct $(CF_3)_2NOCH_2CH(CCl_3)ON(CF_3)_2$ (**5**) (97%) and the rearranged 2:1 adduct $(CF_3)_2NOCH_2CHClCCl_2ON(CF_3)_2$ (**6**) (2.5%); at 75 °C the same products were formed in the ratio 15:77. With 3,3,3-trichloro-2-methylpropene (**4**) and oxyl **1** at 20 °C, rearrangement was more favoured and the products were $(CF_3)_2NOCH_2CMe(CCl_3)ON(CF_3)_2$ (**7**) (56%) and $(CF_3)_2NOCH_2CMeClCCl_2ON(CF_3)_2$ (**8**) (28%), together with $(CF_3)_2NOCCl_2CMe(CH_2Cl)ON(CF_3)_2$ (**9**) (9%) [arising from the alkene $CCl_2{=}CMeCH_2Cl$ (*c.* 10%) present in the reactant olefin]. From the corresponding reactions with the oxadiazapentane $(CF_3)_2NON(CF_3)_2$ (**3**) at *c.* 20 °C, only rearranged products were isolated, i.e. $(CF_3)_2NCH_2CHClCCl_2ON(CF_3)_2$ (**10**) (93%) and $(CF_3)_2NCH_2CMeClCCl_2ON(CF_3)_2$ (**11**) (57%) + $(CF_3)_2NOCCl_2CMeClCH_2Cl$ (**12**) (11.5%).

Introduction

A vicinal chlorine shift in free radicals to give more stable radicals, the so-called Nesmeyanov rearrangement, was first authenticated in 1951 when it was reported that addition of hydrogen bromide to 3,3,3-trichloropropene (**2**) under photochemical or peroxide-initiated conditions gave the rearranged 1:1 adduct $CH_2BrCHClCHCl_2$ [1], i.e.

$$Br^{\cdot} + CH_2{=}CHCCl_3 \longrightarrow CH_2BrC\dot{H}CCl_3 \longrightarrow$$
(2)
$$CH_2BrCHCl\dot{C}Cl_2 \xrightarrow{HBr} CH_2BrCHClCHCl_2$$

Subsequent work has provided many examples of such 1,2-chlorine shifts, e.g. ref. 2, and the rearrangement has been postulated to proceed through a bridged intermediate or transition state in which the odd electron is accommodated in a chlorine d-orbital [1, 2]. An alternative mechanism involving elimination of a chlorine atom, followed by re-addition to the resulting alkene, could be important at higher temperatures when β-scission of chlorine would be expected to be more facile. Indeed, it has been suggested that all vicinal halogen rearrangements occur by this mechanism [3].

As part of a general study of free-radical rearrangement reactions initiated by $(CF_3)_2NO\cdot$ and $(CF_3)_2N\cdot$ radical attack on organic substrates, the reactions of oxyl **1** and the oxadiazapentane **3** with 3,3,3-trichloropropene (**2**) and 3,3,3-trichloro-2-methylpropene (**4**) have been investigated.

$(CF_3)_2NO\cdot$ (**1**) $\quad CH_2{=}CHCCl_3$ (**2**)

$(CF_3)_2NON(CF_3)_2$ (**3**) $\quad CH_2{=}CMeCCl_3$ (**4**)

Experimental

Starting materials

Oxyl **1** (96%) was prepared by oxidation of the hydroxylamine $(CF_3)_2NOH$ with potassium permanganate and sulphuric acid [4], and was converted into the oxadiazapentane **3** (82%) by reaction with trifluoronitrosomethane (2:1 molar ratio) [4]. The reactant alkenes **2** and **4** + **13** (ratio *c.* 90:10; ^1H NMR spectroscopy) were prepared as follows:

(i) $CCl_3Br + CH_2{=}CH_2 \xrightarrow[170\text{–}180\ °C]{(PhCO)_2O_2}$

$CH_2BrCH_2CCl_3$ (67%) $\xrightarrow{KOH/MeOH}$

$CH_2{=}CHCCl_3$ (**2**) (61%) [5]

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(ii) $HOCH_2CHMeCCl_3 \xrightarrow[(ii)\ PhNMe_2]{(i)\ SOCl_2}$

$CH_2{=}CMeCCl_3$ (**4**) + $CH_2ClCMe{=}CCl_2$ (**13**) (30%) in the ratio *c.* 90:10 [6]

General techniques

The reactions involving compounds **1** and **3** were carried out *in vacuo* in Rotaflo tubes (*c.* 300 cm^3) unless stated otherwise. Products were separated by fractional condensation *in vacuo* or by preparative-scale GLC methods [Pye 104 instrument using columns (2 m) packed with Silicone SE30 oil, Apiezon L (APL) grease or trixylyl phosphate (TXP) (20%–25% w/w) on acid-washed Celite] and were examined by IR spectroscopy (Perkin-Elmer 197 instrument), ^1H NMR spectroscopy [Hitachi R20A (60.9 MHz) or Varian Associates HA100 (100.0 MHz) spectrometers; internal reference tetramethylsilane], ^{19}F NMR spectroscopy [Hitachi R20A (56.46 MHz) or Varian HA100 (94.1 MHz) instruments; external reference trifluoroacetic acid] and mass spectrometry (AEI MS902 instrument with an electron beam energy of 70 eV). The NMR spectra were recorded as solutions in $CDCl_3$ and chemical shifts to low field of reference are designated positive.

Molecular weights of gases were measured using Regnault's method and boiling points were determined by Siwoloboff's method.

Reactions of bis(trifluoromethyl)amino-oxyl (1)

(a) With 3,3,3-trichloropropene (2) at room temperature

A mixture of the oxyl **1** (4.67 g, 27.7 mmol) and 3,3,3-trichloropropene (**2**) (2.10 g, 14.7 mmol), stored *in vacuo* at room temperature (6 d), gave a volatile fraction identified (IR spectroscopy) as mainly unchanged alkene **2** (0.12 g, 0.83 mmol, 6% recovered) contaminated with small amounts of bis(trifluoromethyl)amine and *N,N*-bis(trifluoromethyl)hydroxylamine, and a non-volatile fraction (6.64 g) which was separated into its two components (ratio 44:1) by preparative-scale GLC (2 m SE30 at 120 °C). One component was identified as 1,2-bis[bis(trifluoromethyl)amino-oxy]-3,3,3-trichloropropane (**5**) (nc) (6.40 g, 13.3 mmol, 97%) (Analysis: Found: C, 17.7; H, 0.5; Cl, 22.4; N, 6.0; F, 47.9%. $C_7H_3Cl_3F_{12}N_2O_2$ requires: C, 17.5; H, 0.6; Cl, 21.9; N, 5.8; F, 47.5%), b.p. 171 °C. ^1H NMR δ: *c.* 4.7 (complex, $\rangle CHO-$ and $-CH_2O-$) ppm. ^{19}F NMR δ: +11.3 [s, 6F, $CHON(CF_3)_2$]; +7.8 [s, 6F, $CH_2ON(CF_3)_2$] ppm. MS *m/z*: 363 [7.0%, $[M-CCl_3)^+$]; 216 and 218 (14.9, $C_3HClF_6NO^+$); 182 [100.0, $CH_2ON(CF_3)_2^+$]; 144/146/148/150 (13.0, $C_3H_3Cl_3^+$); 131/133/135/137 (31.1, $C_2H_2Cl_3^+$); 130/132/134/136 (17.8, $C_2HCl_3^+$); 117/119/121/123 (8.0, CCl_3^+); 109/111/113 (55.0, $C_3H_3Cl_2^+$); 95/97/99 (30.7, $C_2HCl_2^+$); 83/85/87 (18.2, $CHCl_2^+$); 69 (72.8, CF_3^+). IR ν_{max} (cm^{-1}): 3000–2910 (w, C–H str.); 1300–1206 (vs, C–F str.); 1062 and 1047 (s, C–O–N str.); 966 (s, C–N str.); 840–790 (s, C–Cl str.); 710 (s, CF_3 def.). The second component was 1,3-bis[trifluoromethyl)amino-oxy]-2,3,3-trichloropropane (**6**) (0.15 g, 0.3 mmol, 2.5%) (see next experiment).

(b) With 3,3,3-trichloropropene (2) at 75 °C

A mixture of oxyl **1** (3.32 g, 19.7 mmol) and 3,3,3-trichloropropene (**2**) (1.34 g, 9.2 mmol), heated *in vacuo* in a Pyrex bulb (*c.* 10 dm^3) at 75 °C (6 d), gave a volatile fraction (0.24 g), which was shown (IR and ^{19}F NMR spectroscopy) to consist mainly of unchanged oxyl **1** (*c.* 0.20 g, *c.* 1.2 mmol, *c.* 6% recovered) and a small amount of *N,N*-bis(trifluoromethyl)hydroxylamine, and a non-volatile liquid (4.41 g) which was shown by GLC (2 m TXP at 130 °C and 2 m SE30 at 120 °C) to contain two major components (ratio 5:26) and four minor components. The major components were separated by preparative-scale GLC (2 m SE30 at 120 °C) and identified as the 2:1 adduct **5** (0.63 g, 1.3 mmol, 15%) and the rearranged 2:1 adduct 1,3-bis[bis(trifluoromethyl)amino-oxy]-2,3,3-trichloropropane (**6**) (nc) (3.39 g, 7.0 mmol, 77%) (Analysis: Found: C, 17.8; H, 0.6; Cl, 21.9; N, 6.0%. $C_7H_3Cl_3F_{12}N_2O_2$ requires: C, 17.5; H, 0.6; Cl, 21.9; N, 5.8%), b.p. 174 °C. ^1H NMR δ: 4.68 (dd, 1H CHCl, $J=9$ and 2 Hz); 4.32 (complex, 2H, $-CH_2O-$) ppm. ^{19}F NMR δ: +11.9 [s, 6F, $(CF_3)_2NOCCl_2$]; +7.8 [s, 6F, $(CF_3)_2NOCH_2$] ppm. MS *m/z*: 445/447/449 [1.0%, $(M-Cl)^+$]; 409/411 [1.9, $(M-HCl_2)^+$]; 312/314/316/318 {39.4, $[M-(CF_3)_2NO]^+$}; 250/252/254 [18.9, $(CF_3)_2NOCCl_2^+$]; 230/232 {3.9, $[M-(CF_3)_2NOCCl_2]^+$}; 216/218 (17.3, $C_3HClF_6NO^+$); 182 [57.9, $(CF_3)_2NOCH_2^+$]; 168 [12.4, $(CF_3)_2NO^+$]; 150 (16.3, $C_2HF_5NO^+$); 144/146/148/150 (19.8, $C_3H_3Cl_3^+$); 131/133/135/137 (20.1, $C_2H_2Cl_3^+$); 125/127/129 (29.8, $C_3H_3Cl_2O^+$); 95/97/99 (53.3, $C_2HCl_2^+$); 77/79 (15.3, $C_2H_2ClO^+$); 69 (100.0, CF_3^+); 63/65 (35.3, $CClO^+$). IR ν_{max} (cm^{-1}); 3000–2910 (w, C–H str.); 1305–1206 (vs, C–F str.); 1070 and 1050 (s, C–O–N str.); 979 (s, C–N str.); 880–817 (s, C–Cl str.); 715 (s, CF_3 def.).

(c) With 3,3,3-trichloro-2-methylpropene (4)

A mixture of oxyl **1** (3.23 g, 19.2 mmol), 3,3,3-trichloro-2-methylpropene (**4**) (1.395 g, 8.73 mmol) and 1,1,3-trichloro-2-methylpropene (**13**) (0.155 g, 0.97 mmol), stored *in vacuo* at room temperature (1 h), gave (i) a −196 °C fraction (0.04 g) (Found: M, 55) shown (IR spectroscopy) to consist of unchanged oxyl **1** (0.02 g, 0.1 mmol, 0.5% recovered) and hydrogen chloride (0.02 g, 0.6 mmol, 6%), (ii) *N,N*-bis(trifluoromethyl)-

hydroxylamine (0.07 g, 0.4 mmol, 2% based on oxyl), which condensed at −78 °C and (iii) a non-volatile liquid residue (4.56 g) which was shown by GLC (2 m TXP at 120 °C) to contain four components in the ratio 2:73:8:2.

The major components were separated by preparative-scale GLC (2 m TXP at 120 °C) and identified as follows. (i) A mixture of 1,2-bis[bis(trifluoromethyl)-amino-oxy]-3,3,3-trichloro-2-methylpropane (**7**) (nc) and 1,3-bis[bis(trifluoromethyl)amino-oxy]-1,1,2-trichloro-2-methylpropane (**8**) (nc) (4.03 g, 8.1 mmol, 84% based on oxyl) (Analysis: Found: C, 19.7; H, 1.1; Cl, 21.5; N, 6.0%. $C_8H_5Cl_3F_{12}N_2O_2$ requires: C, 19.4; H, 1.0; Cl, 21.5; H, 5.7%) in the ratio 67:33. ^{1}H NMR: bands for compound **7** at δ 4.47 and 4.33 (AB, 2H, $-CH_AH_BO-$, $J_{AB}=11$ Hz) and 1.74 (s, 3H, CH_3) ppm and for compound **8** at δ 4.62 and 4.54 (AB, 1H, $-CH_AH_BO-$, $J_{AB}=11$ Hz) and 1.82 (s, 1.5H, CH_3) ppm. ^{19}F NMR: bands for compound **7** at $\delta+10.6$ [complex, 6F, $-CON(CF_3)_2$] and +7.9 [s, 6F, $CH_2ON(CF_3)_2$] ppm and for compound **8** at $\delta+12.4$ [s, 3F, $CCl_2ON(CF_3)_2$] and +7.9 [s, 3F, $CH_2ON(CF_3)_2$] ppm. MS *m/z*: 459/461/463 [8.9%, $(M-Cl)^+$]; 377 [5.2, $(M-CCl_3)^+$]; 326/328/330/332 {26.3, $[M-(CF_3)_2NO]^+$}; 312/314/316/318 {10.3, $[M-(CF_3)_2NOCH_2]^+$}; 290/292/294 {37.4, $[M-(CF_3)_2NO-HCl]^+$}; 250/252/254 [1.9, $(CF_3)_2NOCCl_2^+$]; 244/246 {5.9, $[M-(CF_3)_2NOCCl_2]^+$}; 216/218 (99.1, $C_3HClF_6NO^+$); 182 [85.0, $(CF_3)_2NOCH_2^+$]; 158/160/162/164 (35.2, $C_4H_5Cl_3^+$); 144/146/148/150 (27.6, $C_3H_3Cl_3^+$); 123/125/127 (50.0, $C_4H_5Cl_2^+$); 117/119/121/123 (1.2, CCl_3^+); 109/111/113 (25.9, $C_3H_3Cl_2^+$); 69 (78.9, CF_3^+); 43 (100.0, $C_2H_3O^+$). IR ν_{max} (cm^{-1}) 3000–2900 (w, C−H str.); 1333–1205 (vs, C−F str.); 1070–1045 (s, C−O−N str.); 980–940 (s, C−N str.); 836–809 (s, C−Cl str.); 710 (s, CF_3 def.). (ii) 1,2-Bis[bis(trifluoromethyl)amino-oxy]-1,1,3-trichloro-2-methylpropane (**9**) (nc) (0.45 g, 0.9 mmol, 9% based on oxyl) (Analysis: Found: C, 19.5; H, 1.0; N, 5.9%. $C_8H_5Cl_3F_{12}N_2O_2$ requires: C, 19.4; H, 1.0; N, 5.7%). ^{1}H NMR δ: 3.96 (br., 2H, CH_2Cl); 1.75 (s, 3H, CH_3) ppm. ^{19}F NMR δ: +12.4 [s, 6F, $CCl_2ON(CF_3)_2$]; +10.6 [s, 6F, $-CON(CF_3)_2$] ppm. MS *m/z*: 458/460/462 [4.6%, $(M-HCl)^+$]; 445/447/449 [6.8, $(M-CH_2Cl)^+$]; 326/328/330/332 {30.1, $[M-(CF_3)_2NO]^+$}; 291/293/295 (8.9, $C_6H_5Cl_2F_6NO^+$); 277/279/281 (7.0, $C_5H_3Cl_2F_6NO^+$); 250/252/254 [1.6, $(CF_3)_2NOCCl_2^+$]; 244/246 {6.2, $[M-(CF_3)_2NOCCl_2]^+$}; 216/218 (8.2, $C_3HClF_6NO^+$); 158/160/162/164 (37.2, $C_4H_5Cl_3^+$); 123/125/127 (22.1, $C_4H_5Cl_2^+$); 111/113/115 (25.5, $C_3H_5Cl_2^+$); 69 (33.5, CF_3^+); 49/51 (8.5, CH_2Cl^+); 43 (100.0, $C_2H_3O^+$).

Reactions of perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) (3)

(a) With 3,3,3-trichloropropene (2)

A mixture of oxadiazapentane **3** (2.24 g, 7.0 mmol) and 3,3,3-trichloropropene (**2**) (1.0 g, 6.9 mmol), stored *in vacuo* at room temperature (20 h), gave (i) a volatile fraction (1.32 g) which was shown (IR and ^{19}F NMR spectroscopy) to consist of unchanged oxadiazapentane **3** (1.31 g, 4.0 mmol, 57% recovered) contaminated with trace amounts of bis(trifluoromethyl)amine and *N,N*-bis(trifluoromethyl)hydroxylamine and (ii) a colourless non-volatile liquid (1.92 g) shown by GLC (2 m SE30 at 114 °C) to contain two major components (ratio 58:42). The components were separated by preparative-scale GLC (2 m SE30 at 110 °C) and identified as unchanged 3,3,3-trichloropropene (**2**) (0.56 g, 3.9 mmol, 56% recovered) and 3-bis(trifluoromethyl)amino-1-bis(trifluoromethyl)amino-oxy-1,1,2-trichloropropane (**10**) (nc) (1.30 g, 2.8 mmol, 93%) (Analysis: Found: C, 18.4; H, 0.5; Cl, 22.9; H, 6.0; F, 49.1%. $C_7H_3Cl_3F_{12}N_2O$ requires: C, 18.1; H, 0.6; Cl, 22.6; N, 6.0; F, 49.1%), b.p. 176 °C. ^{1}H NMR δ: 4.37 (dd, 1H, CHCl, $J=10$ and 2 Hz); 4.05 and 3.58 (2 ABd, 2H, $-CH_AH_B$ N−, $J_{AB}=16$ Hz) ppm. ^{19}F NMR δ: +18.6 [s, 6F, $(CF_3)_2NCH_2$]; +11.9 [s, 6F, $(CF_3)_2NOCCl_2$] ppm. MS, *m/z*: 263/265/267 {14.3% $[M-(CF_3)_2NCH_2Cl]^+$}; 250/252/254 [3.6, $(CF_3)_2NOCCl_2^+$]; 214/216 {1.8, $[M-(CF_3)_2NOCCl_2]^+$}; 182 (12.7, $C_3H_2F_6NO^+$); 166 [100.0, $(CF_3)_2NCH_2^+$]; 109/111/113 (3.1, $C_3H_3Cl_2^+$); 78/80 (38.8, $C_2H_3ClO^+$); 69 (51.7, CF_3^+). IR ν_{max} (cm^{-1}); 3020–2980 (w, C−H str.); 1370–1150 (vs, C−F str.); 1045 and 1028 (s, C−O−N str.); 963 (s, C−N str.); 840–790 (s, C−Cl str.); 712 (s, CF_3 def.).

(b) With 3,3,3-trichloro-2-methylpropene (4)

A mixture of oxadiazapentane **3** (2.62 g, 8.2 mmol), 3,3,3-trichloro-2-methylpropene (**4**) (1.233 g, 7.74 mmol) and 1,1,3-trichloro-2-methylpropene (**13**) (0.137 g, 0.86 mmol), stored *in vacuo* at room temperature (8 d), gave (i) a volatile mixture (0.50 g) shown (IR spectroscopy) to consist of hydrogen chloride, bis(trifluoromethyl)amine and *N,N*-bis(trifluoromethyl)hydroxylamine and (ii) a non-volatile liquid (3.49 g) shown by GLC (2 m APL at 100 °C) to contain 10 components of which two were major. The two major components were separated by preparative-scale GLC (2 m APL at 100 °C) to afford the following. (i) 1-Bis(trifluoromethyl)amino-oxy-3-bis(trifluoromethyl)-amino-1,1,2-trichloro-2-methylpropane (**11**) (nc) (2.32 g, 4.9 mmol, 57%) (Analysis: Found: C, 20.3; H, 1.2; N, 6.1; F, 47.8%. $C_8H_5Cl_3F_{12}N_2O$ requires: C, 20.0; H, 1.0; N, 5.8; F, 47.5%). ^{1}H NMR δ: 3.93 [br., 2H, $CH_2N(CF_3)_2$]; 1.81 (s, 3H, CH_3) ppm. ^{19}F NMR δ: +20.2 [s, 6F, $(CF_3)_2NCH_2$]; +12.5 [s, 6F, $(CF_3)_2NOCCl_2$] ppm. MS *m/z*: 277/279/281 {14.4%,

$[M-(CF_3)_2NCH_2Cl]^+$]; 228/230 {6.1, $[M-(CF_3)_2NOCCl_2]^+$}; 182 (12.9, $C_3H_2F_6NO^+$); 166 [100.0, $(CF_3)_2NCH_2^+$]; 158/160/162/164 (5.4, $C_4H_5Cl_3^+$); 133 (5.6, $C_2F_5N^+$); 111/113/115 (5.7, $C_3H_5Cl_2^+$); 95/97/99 (51.6, $C_2HCl_2^+$); 90/92 (17.4, $C_3H_3OCl^+$); 78 (28.8, $C_2H_2F_2N^+$); 69 (54.8, CF_3^+). IR ν_{max} (cm^{-1}): 3010–2915 (w, C–H str.); 1387–1164 (vs, C–F str.); 1029 (s, C–O–N str.); 970 (s, C–N str.); 845–808 (s, C–Cl str.); 712 (s, CF_3 def.). (ii) Impure 1-bis(trifluoromethyl)amino-oxy-1,1,2,3-tetrachloro-2-methylpropane (**12**) (nc) (0.36 g, 1.00 mmol, 11.5%); ^1H NMR δ: 4.10 (br., 2H, CH_2Cl); 2.02 (s, 3H, CH_3) ppm. ^{19}FNMR δ: +13.2 [s, $(CF_3)_2NOCCl_2$] ppm. MS *m/z*: 326/328/330/332 [100.0%, $(M-Cl)^+$]; 312/314/316/318 [2.2, $(M-CH_2Cl)^+$]; 290/292/294 [25.9, $(M-HCl_2)^+$]; 250/252/254 [2.1, $(CF_3)_2NOCCl_2^+$]; 193/195/197/199/201 (39.4, $C_4H_5Cl_4^+$); 158/160/162/164 (29.2, $C_4H_5Cl_3^+$); 157/159/161/163 (50.3, $C_4H_4Cl_3^+$); 144/146/148/150 (25.5, $C_3H_3Cl_3^+$); 123/125/127 (18.6, $C_4H_5Cl_2^+$); 111/113/115 (77.1, $C_3H_5Cl_2^+$); 69 (37.9, CF_3^+); 49/51 (17.6, CH_2Cl^+); 41 (9.3, $C_3H_5^+$); 39 (22.2, $C_3H_3^+$).

Results and discussion

The results obtained from the reaction of oxyl **1** and oxadiazapentane **3** with the alkenes **2** and **4** are summarised in Table 1.

$(CF_3)_2NOCH_2CR(CCl_3)ON(CF_3)_2$
(**5**) R = H
(**7**) R = Me

$(CF_3)_2NOCH_2CRClCCl_2ON(CF_3)_2$
(**6**) R = H
(**8**) R = Me

$(CF_3)_2NOCCl_2CMe(CH_2Cl)ON(CF_3)_2$
(**9**)

$(CF_3)_2NCH_2CRClCCl_2ON(CF_3)_2$
(**10**) R = H
(**11**) R = Me

$(CF_3)_2NOCCl_2CMeClCH_2Cl$
(**12**)

The high-boiling products **5–12** were separated by preparative-scale GLC and were identified by consideration of their ^{19}F NMR and mass spectra (Table 2); compounds **7** and **8** could not be separated and were analysed as a mixture (2:1 molar ratio). The ^1H NMR spectra did not allow a differentiation between rearranged and non-rearranged structures, although they showed absorptions in the expected regions for methylene and methyl or methine protons.

From the data it is clear that products **5–8** contain a $(CF_3)_2NOCH_2$ grouping, products **6** and **8–12** contain a $(CF_3)_2NOCCl_2$ grouping, products **10** and **11** contain a $(CF_3)_2NCH_2$ grouping and products **5, 7** and **9** contain a second $(CF_3)_2NO$ group. Compounds **5** and **7** also contain a CCl_3 group and compounds **9** and **12** a CH_2Cl group. Confirmation that compound **12** was a tetrachloride was obtained from the existence of a mass spectral peak at *m/z* 193 {39%, $C_4H_5Cl_4^+$, i.e. $[M-(CF_3)_2NO]^+$}.

Products **5–8** obtained from the reactions of oxyl **1** were formed via the intermediate radical **14** and the rearranged radical **15**; the remaining substituted alkane **9**, the 2:1 adduct of oxyl **1** and the alkene $CCl_2=CMeCH_2Cl$ **13** (present as an impurity), arose via the intermediate radical **16** (Scheme 1).

Rearrangement of the secondary radical **14a** to radical **15a** via a 1,2-chlorine shift did not compete effectively at room temperature with the scavenging of radical **14a** by oxyl **1**; at 75 °C, however, rearrangement was the major reaction pathway.

The driving force for rearrangement is the formation of a more stable radical and it would be expected that rearrangement of the secondary radical **14a** would be more facile than that of the tertiary radical **14b**. How-

TABLE 1. Reactions of $(CF_3)_2NO\cdot$ and $(CF_3)_2NON(CF_3)_2$ with the alkenes $CH_2=CRCCl_3$ (R = H and Me)

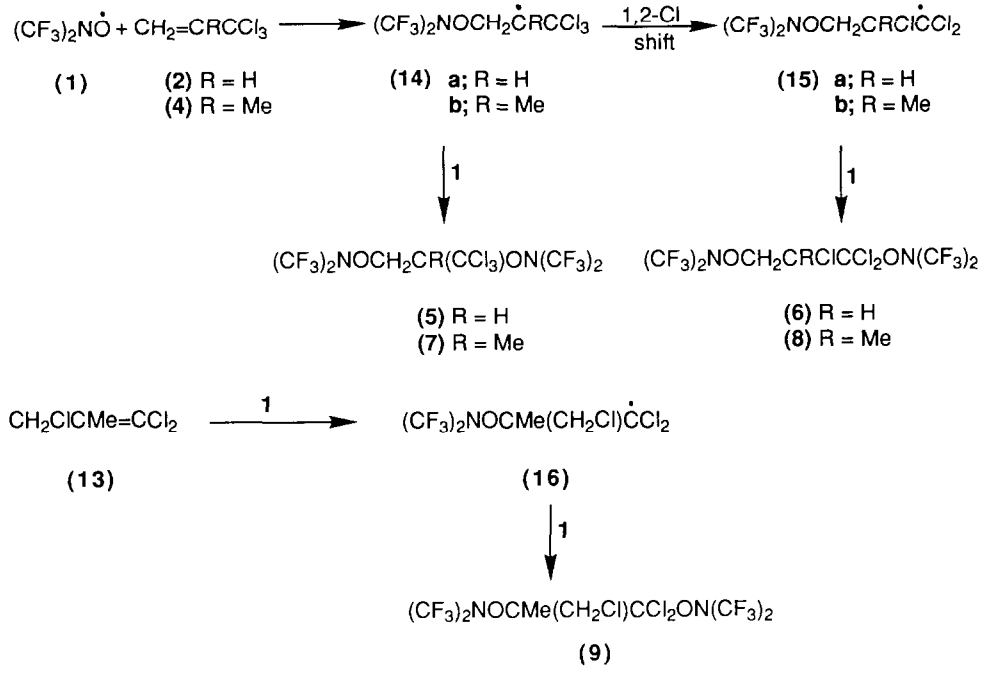
Reactants	Molar ratio	Time (h)	Temperature (°C)	Recovered reactants (%)	Products (%)[b,c]
1+**2**	*c.* 2:1	144	*c.* 20	**2**(6)	**5**(97); **6**(2.5)
1+**2**	*c.* 2:1	144	75	**1**(6)	**5**(15); **6**(77)
1+**4**[a]	*c.* 2:1	1	*c.* 20	**1**(0.5)	**7**(56); **8**(28); **9**(9)[d]
3+**2**	*c.* 1:1	20	*c.* 20	**2**(56); **3**(57)	**10**(93)
3+**4**[a]	*c.* 1:1	192	*c.* 20		**11**(57); **12**(11.5)[e]

[a]Alkene **4** contained $CCl_2=CMeCH_2Cl$ (**13**) (*c.* 10%).
[b]Yields based on reactants **1** or **3** consumed.
[c]Small amounts of $(CF_3)_2NH$ and/or $(CF_3)_2NOH$ also formed.
[d]HCl (6%) and two minor high-boiling products also formed.
[e]HCl and eight minor high-boiling products also formed.

TABLE 2. ^{19}F NMR chemical shifts (ppm relative to TFA) and mass spectral peaks for products **5–12**

Compound	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	Assignment
	+7.8	+7.8	+7.8	+7.8					$(CF_3)_2NOCH_2$
	+11.3								$(CF_3)_2NOCHCl$
δ_F		+11.9		+12.4	+12.4	+11.9	+12.5	+13.2	$(CF_3)_2NOCCl_2$
			+10.6		+10.6				$(CF_3)_2NOCMe$
						+18.6	+20.2		$(CF_3)_2NCH_2$
					445			312	$(M-CH_2Cl)^+$
					(7)			(2)	
	363		377						$(M-CCl_3)^+$
	(7)		(5)						
		250		250	250	250		250	$(CF_3)_2NOCCl_2^+$
		(19)		(2)	(2)	(4)		(2)	
		230		244	244	214	228	111	$[(M-CF_3)_2NOCCl_2]^+$
		(4)		(6)	(6)	(2)	(6)	(77)	
m/z[a]	182	182	182	182					$(CF_3)_2NOCH_2^+$
(%)	(100)	(58)	(85)	(85)					
						166	166		$(CF_3)_2NCH_2^+$
						(100)	(100)		
	117		117						CCl_3^+
	(8)		(11)						
					49			49	CH_2Cl^+
					(9)			(18)	

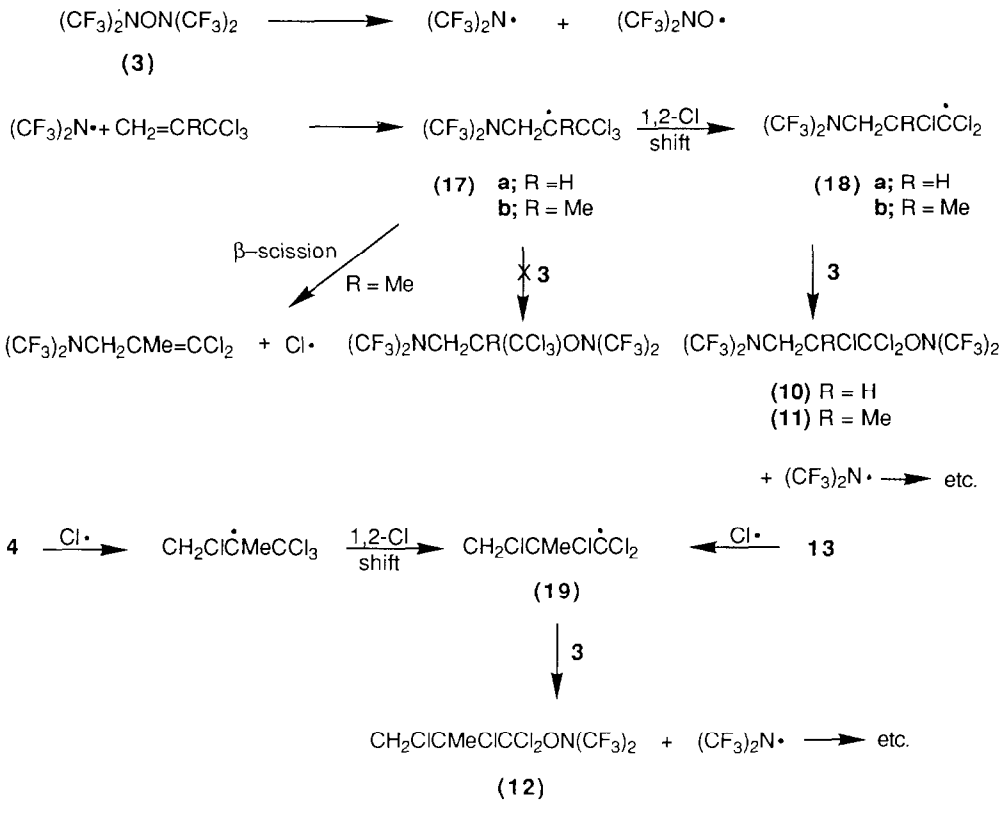
[a]For peaks due to ions containing chlorine, only the ^{35}Cl peak is given.



Scheme 1.

ever, at room temperature the opposite was observed, i.e. rearrangement of radical **14b** to radical **15b** (28%) was favoured over rearrangement of radical **14a** to radical **15a** (2.5%). It is possible that this observation is a consequence of increased steric hindrance towards coupling with oxyl **1** in the tertiary radical **14b** relative to the secondary radical **14a**, thus allowing rearrangement of **14b** to **15b** to become more favoured.

It is well established that 1:1 adduct formation between the oxadiazapentane **3** and alkenes involves a radical-chain mechanism initiated by homolytic N–O bond fission, followed by $(CF_3)_2N\cdot$ radical attack on



Scheme 2.

the alkene and then chain transfer by attack of the resulting radical on **3** at oxygen [7–9]. In certain cases, especially at elevated temperature, the 2:1 adduct of oxyl **1** and the alkene can be formed as a by-product, e.g. with tetrachloroethene [10].

The reaction between **3** and alkene **2** was clean and gave the rearranged 1:1 adduct **10** in high yield via the radicals **17a** and **18a**. In contrast, reaction of **3** with the 2-methylalkene **4** was somewhat complex and afforded a mixture of the compounds HCl, $(CF_3)_2NH$ and $(CF_3)_2NOH$, together with a high-boiling mixture comprising of 10 components from which only the major products, the rearranged 1:1 adduct **11** and tetrachloride **12**, could be separated by GLC methods and identified. Compounds **10–12** are considered to have been formed as shown in Scheme 2.

Since only rearranged 1:1 adducts, i.e. **10** and **11**, were isolated, it is evident that the chain-transfer reactions involving the initially-formed radicals **17** and oxadiazapentane **3** are slower than those between radicals **14** and oxyl **1**, thus allowing rearrangement of radicals **17** to radicals **18** via a 1,2-chlorine shift, prior to chain transfer with **3**, to be the major reaction pathway.

The formation of tetrachloride **12** requires a chlorine atom attack on alkene **4** and/or alkene **13** to have occurred to give the intermediate radical **19**, which then reacts with oxadiazapentane **3** at oxygen. It is probable that the chlorine atoms arose by β-scission of chlorine from the radical **17b**; the presence of hydrogen chloride in the products from the reaction of oxyl **1** with alkene **4** indicates that β-scission of chlorine from radical **14b** also occurs to some extent.

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