Journal of Fluorine Chemistry, *66* (1994) 271–277

The reactions of mercury(II) perfluoro-2,5-diazahexane 2,5-dioxyl and perfluoro-2,5-diazahexane-2,5-diol with halogenoalkanes, acid chlorides and dichlorosilanes

Michael J. Green and Anthony E. Tipping*

Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD (UK)

(Received December 3, 1992; accepted April 8, 1993)

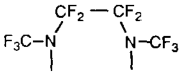
Abstract

Treatment of the title mercurial (**2**) with the halogenoalkanes MeI, MeBr and EtI, or the acid chlorides MeCOCl and CF_3COCl, gives the compounds $RON(CF_3)CF_2CF_2N(CF_3)OR$ (R = Me, Et, MeCO and CF_3CO) in good yield; reaction does not take place with the halides CF_3CH_2I or $BrCH_2CH_2Br$. Reaction involving the di-iodoalkanes CH_2I_2 and $ICH_2CH_2CH_2I$ affords the heterocycle $\overline{ON(CF_3)CF_2CF_2N(CF_3)OC}H_2$ and the copolymer $[ON(CF_3)CF_2CF_2N(CF_3)OCH_2CH_2CH_2]_n$, respectively, while from the dichlorosilanes Me_2SiCl_2 and $\overline{CH_2CH_2CH_2Si}Cl_2$, the products are the seven-membered ring heterocycle $\overline{ON(CF_3)_2CF_2CF_2N(CF_3)OSi}Me_2$ and the spiro compound $\overline{ON(CF_3)CF_2CF_2N(CF_3)OS}\underline{iCH_2CH_2CH}_2$, respectively. Perfluoro-2,5-diazahexane-2,5-diol (**3**) undergoes reactions with the halides Me_2SiCl_2 and CF_3COCl in the presence of quinoline to give the same products as formed from mercurial **2**, but reaction does not take place with iodoethane; the reaction with the acid chloride CF_3COCl can also be effected using potassium fluoride in place of quinoline.

Introduction

The reactions of the oxyl $(CF_3)_2NO\bullet$ with both organic and inorganic compounds have been investigated extensively and certain of its derivatives, i.e. the sodium salt $(CF_3)_2NONa$ [1], the mercurial $[(CF_3)_2NO]_2Hg$ [2] and adducts of the hydroxylamine $(CF_3)_2NOH$ with KF or CsF [3], have also been used to synthesise many compounds containing the $(CF_3)_2NO$ group. In contrast the chemistry of the analogue, perfluoro-2,5-diazahexane 2,5-dioxyl (**1**) and its derivatives has met with only limited attention. In reactions where the oxyl $(CF_3)_2NO\bullet$ gives 2:1 adducts, the dioxyl **1**, because of its bifunctionality, affords heterocyclic compounds, e.g. with sulphur dioxide [4], or copolymers or mixtures of copolymers and heterocycles, e.g. with alkenes [5–7]. The mercurial **2** [8] and the diol **3** [6] have been synthesised from dioxyl **1** by reaction with mercury and hydrogen bromide, respectively, and reactions of mercurial **2** with inorganic halides, e.g. $SOCl_2$ and $COCl_2$ [8], have been studied.

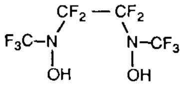
In the present work, the reactions of mercurial **2** and diol **3** (in the presence of KF or quinoline) with halogenoalkanes, monoacid chlorides and dichlorosilanes have been investigated.



(1)

$-\!\!\![ON(CF_3)CF_2CF_2N(CF_3)OHg]_n$

(2)



(3)

Experimental

Starting materials

Mercury(II) perfluoro-2,5-diazahexane 2,5-dioxyl (**2**) was prepared (*c.* 60%) on a small scale (1.5–2.5 g) by reaction of a known weight of mercury (1–2 g) with an excess of perfluoro-2,5-diazahexane 2,5-dioxyl (**1**) in $CF_2ClCFCl_2$ solvent contained *in vacuo* in a preweighed Pyrex tube fitted with a Rotaflo tap (*c.* 100 cm^3) which was then shaken at room temperature in the dark (21 d) [8]. The volatile material was removed *in vacuo* and the quantities of unreacted mercury and product **2** were determined by reweighing the tube. Perfluoro-2,5-diazahexane-2,5-diol (**3**) was made in high yield by reaction of dioxyl **1** with hydrogen bromide [6] in $CF_2ClCFCl_2$ solvent contained *in vacuo* in a preweighed Rotaflo tube (*c.* 300 cm^3) at 0 °C (*c.* 0.5 h). After careful removal of the volatile material at 0 °C [to avoid loss of the product diol **3**], the yield of diol **3** was determined by reweighing the tube.

---

*Author to whom correspondence should be addressed.

SSDI 0022-1139(93)02914-Z

The halogenoalkanes, acid chlorides and dichlorodimethylsilane were commercial samples and 1,1-dichloro-1-silacyclobutane [13] was a research sample available in this Department; the purity of each was determined (IR, NMR spectroscopy) before use.

General techniques

Reactions of mercurial **2** were carried out *in vacuo* in the tubes (*c.* 100 cm^3) in which it was prepared, by condensing the appropriate co-reactant *in vacuo* into the tubes cooled to −196 °C, then warming the tubes to room temperature and shaking them for the stated length of time. For reactions involving diol **3**, the tubes in which it was prepared were opened, quinoline (or potassium fluoride and $CF_2ClCFCl_2$ solvent) was added and the tubes evacuated and then shaken at room temperature (5–10 min for the quinoline reactions and 0.5 h for the KF reactions). The solvent, if present, was removed *in vacuo*, the tubes cooled to −196 °C and the co-reactant condensed in. After warming to room temperature, the tubes were shaken for the specified period.

After reaction was completed, the volatile material was removed *in vacuo* from the tubes and separated by fractional condensation *in vacuo* in a vacuum system with the vapour passed at low pressure (1–2 mmHg) through traps cooled to successively lower temperatures. Any polymeric material remaining in the tubes was extracted ($CF_2ClCFCl_2$, 4×15 cm^3) and the solvent removed from the solution by pumping *in vacuo* to constant weight.

The products were examined by IR spectroscopy (Perkin-Elmer 137 or 257 instruments), ^{1}H NMR [Perkin-Elmer R10 (60.0 MHz) spectrometer; external reference Me_4Si] and ^{19}F NMR spectroscopy [Perkin-Elmer R10 (56.46 MHz) or Varian Associates HA100 (94.12 MHz) instruments; external reference CF_3CO_2H] and mass spectrometry (A.E.I. MS 902 spectrometer; electron beam energy 70 eV). The NMR spectra were recorded using neat liquids or solutions (in $CF_2ClCFCl_2$) as stated in the text; chemical shifts to low field of reference are designated positive.

Boiling points were determined by Siwoloboff's method and refractive indices were measured on an Abbé refractometer.

Reactions of mercury(II) perfluoro-2,5-diazahexane 2,5-dioxyl (2)

(a) With iodomethane

Iodomethane (1.40 g, 7.32 mmol) was condensed *in vacuo* on to mercurial **2** (1.74 g, 3.49 mmol) [prepared from mercury (1.14 g), dioxyl **1** (4.09 g, 13.72 mmol) in 1,1,2-trichlorotrifluoroethane (12 cm^3) which was stored (21 d) and the volatile material removed *in vacuo*] and the tube shaken at room temperature (18 h). The volatile products were removed *in vacuo* [leaving a red solid presumed to be HgI_2] and separated by fractional condensation *in vacuo* to give (i) a −96 °C fraction identified as unchanged iodomethane (0.09 g, 0.63 mmol, 8.5% recovered) and (ii) a −23 °C fraction, which was identified as 4,4,5,5-tetrafluoro-3,6-bis(trifluoromethyl)2,7-dioxa-3,6-diazaoctane (**4a**) (nc) (0.98 g, 2.99 mmol, 89.5%) (Analysis: Found: C, 21.8; H, 1.9; F, 57.5; N, 8.4%; M^+, 328. $C_6H_6F_{10}N_2O_2$ requires: C, 21.95; H, 1.8; F, 57.9; N, 8.5%; M, 328), b.p. 135 °C; n_D^{20} 1.3140. IR $\nu_{max.}$ (cm^{-1}): 3012 and 2959 (m, C−H str.); 1271–1168 (vs, C−F str.); 1055 (s, N−O str.); 704 (s, CF_3 def.). ^{1}H NMR (neat) δ: 4.39 (s, OCH_3) ppm. ^{19}F NMR δ: +10.8 (t, 3F, CF_3N, J=12.9 Hz); −27.3 (q, CF_2N, J=12.9 Hz) ppm. MS m/z: 328 (0.7%, M^+); 309 [3.7, $(M-F)^+$]; 214 (16.1, $C_4H_3FNO^+$); 164 (100.0, $M^+/2$); 114 (13.6, $C_2F_4N^+$); 69 (63.3, CF_3^+); 31 (11.7, CH_3O^+).

(b) With bromomethane

Bromomethane (0.95 g, 10.0 mmol) was condensed *in vacuo* on to mercurial **2** (2.09 g, 4.19 mmol) (prepared as in the first experiment) and the tube shaken (5 d). The volatile products were separated by fractional condensation *in vacuo* to give (i) a −140 °C fraction identified as unchanged bromomethane (0.49 g, 5.16 mmol, 51.5% recovered) and (ii) a −23 °C fraction identified as the diaza-octane **4a** (0.72 g, 2.20 mmol, 91%).

(c) With iodoethane

Iodoethane (0.89 g, 5.71 mmol) was condensed *in vacuo* on to mercurial **2** (2.09 g, 4.19 mmol) and the tube shaken (20 h) to give as the only volatile material 5,5,6,6-tetrafluoro-4,7-bis(trifluoromethyl)-3,8-dioxa-4,7-diazadecane (**4b**) (nc) (0.94 g, 2.64 mmol, 92.5%) (Analysis: Found: C, 26.9; H, 2.8; F, 53.2; N, 7.8%; M^+, 356. $C_8H_{10}F_{10}N_2O_2$ requires: C, 26.95; H, 2.8; F, 53.4; N, 7.9%; M, 356), b.p. 150 °C; n_D^{20} 1.3267. IR $\nu_{max.}$ (cm^{-1}): 3003 and 2941 (m, C−H str.) 1276–1153 (vs, C−F str.); 1070 (s, C−O str.); 1047 and 1020 (s, N−O str.); 710 (s, CF_3 def.). ^{1}H NMR (neat) δ: 4.71 (q, 2H, CH_2O, J=7.2 Hz); 1.71 (t, 3H, CH_3, J=7.2 Hz) ppm. ^{19}F NMR δ: +11.2 (t, 3F, CF_3N, J=12.4 Hz); −26.4 (br., 2F, CF_2N) ppm. MS m/z: 356 (0.5%, M^+); 337 [1.8, $(M-F)^+$]; 328 [23.1, $(M-C_2H_4)^+$]; 308 (44.4, $C_6H_5F_9N_2O_2^+$); 300 [14.2, $(M-2C_2H_4)^+$]; 280 (96.5, $C_4HF_9N_2O_2^+$); 181 (59.7, $C_3HF_6NO^+$); 150 (26.9, $C_2HF_5NO^+$); 114 (22.5, $C_2F_4N^+$); 69 (100.0, CF_3^+); 45 (21.2, $C_2H_5O^+$); 44 (20.1, $C_2H_4O^+$ and CH_2NO^+); 43 (36.2, $C_2H_3O^+$ and $CHNO^+$); 30 (25.6, CH_2O^+).

(d) With 1,1,1-trifluoroiodoethane

A mixture of mercurial **2** (1.88 g, 3.76 mmol) and 1,1,1-trifluoroiodoethane (2.01 g, 9.57 mmol), heated at 50 °C (72 h), gave as a volatile material (i) a −196 °C fraction, identified as trifluoronitrosomethane (0.02 g, 0.19 mmol, 5%) and (ii) a −78 °C fraction, identified as unchanged iodoalkane (1.98 g, 9.43 mmol, 98.5% recovered).

(e) With acetyl chloride

A mixture of mercurial **2** (2.30 g, 4.60 mmol) and acetyl chloride (0.77 g, 9.81 mmol), shaken at room temperature (20 h), gave as a volatile material (i) unchanged acetyl chloride (0.09 g, 9% recovered), which condensed at −78 °C and (ii) a 0 °C fraction, identified as 1,6-bis(acetyl)-3,3,4,4-tetrafluoro-2,5-bis(trifluoromethyl)-1,6-dioxa-2,5-diazahexane (**4c**) (nc) (1.44 g, 3.75 mmol, 87%) (Analysis: Found: C, 25.1; H, 1.5; F, 49.3%. $C_8H_6F_{10}N_2O_4$ requires: C, 25.0; H, 1.6; F, 49.5%), b.p. 188 °C; n_D^{20} 1.3380. IR $\nu_{max.}$ (cm^{-1}): 2959 (w, C−H str.); 1830 (s, C=O str.); 1276–1153 (vs, C−F str.); 1079 (s, C−O str.); 1043 (s, N−O str.); 710 (s, CF_3 def.). ^{1}H NMR (neat) δ: 2.01 (s, CH_3) ppm. ^{19}F NMR δ: +12.0 (s, 6F, $2CF_3N$); −26.2 (s, 4F, NCF_2CF_2N) ppm. MS *m/z*: 323 (0.1%, $C_6HF_{10}N_2O_2^+$); 281 (0.4, $C_4H_2F_9N_2O_2^+$); 150 (2.5, $C_2HF_5NO^+$); 114 (5.0, $C_2F_4N^+$); 69 (19.0 CF_3^+); 43 (100.0 $C_2H_3O^+$); 28 (16.2, CO^+).

(f) With trifluoroacetyl chloride

A mixture of mercurial **2** (1.76 g, 3.52 mmol) and trifluoroacetyl chloride (1.33 g, 10.04 mmol) shaken at room temperature (7 d) gave as a volatile material (i) unchanged trifluoroacetyl chloride (0.40 g, 3.02 mmol, 30% recovered) which condensed at −196 °C and (ii) a −23 °C fraction, identified as 1,6-bis(trifluoroacetyl)-3,3,4,4-tetrafluoro-2,5-bis(trifluoromethyl)-1,6-dioxa-2,5-diazahexane (**4d**) (nc) (1.63 g, 3.31 mmol, 94.5%) (Analysis: Found: C, 19.5; F, 61.7%. $C_8F_{16}N_2O_4$ requires: C, 19.5; F, 61.8%), b.p. 124 °C. IR $\nu_{max.}$ (cm^{-1}): 1861 (vs, C=O str.); 1288–1182 (vs, C−F str.); 1088 (s, C−O str.); 1054 (s, N−O str.); 715 (s, CF_3 def.). ^{19}F NMR (neat) δ: +11.2 (s, 6F, $2CF_3N$); +7.0 (s, 6F, $2CF_3C{=}O$); −27.5 (br., 4F, NCF_2CF_2N) ppm. MS *m/z*: 473 [0.3%, $(M-F)^+$]; 379 [2.5, $M-CF_3CO_2)^+$]; 296 (5.7, $C_5F_{10}NO_2^+$); 218 (15.0, $C_3F_8NO^+$); 130 (7.8, $C_2F_4NO^+$); 114 (10.4, $C_2F_4N^+$); 97 (36.5, $C_2F_3O^+$); 69 (100.0, CF_3^+); 44 (12.6, CO_2^+); 28 (16.4, CO^+).

(g) With di-iodomethane

A mixture of mercurial **2** (2.28 g, 4.56 mmol) and di-iodomethane (0.89 g, 3.32 mmol), shaken at room temperature (35 d), gave as a volatile material the sole product 3,3,4,4-tetrafluoro-2,5-bis(trifluoromethyl)-1,6-dioxa-2,5-diazacycloheptane (**5**) (nc) (0.43 g, 1.38 mmol, 41.5%) (Analysis: Found: C, 19.2; H, 0.4; F, 60.8; N, 8.8%; M$^+$, 312. $C_5H_2F_{10}N_2O_2$ requires: C, 19.2; H, 0.6; F, 60.9; N, 9.0%; M, 312), b.p. 111 °C; n_D^{20} 1.3073. IR $\nu_{max.}$ (cm^{-1}): 2985 and 2915 (w, C−H str.); 1276–1190 (vs, C−F str.); 1090 and 1070 (s, C−O str.); 1043 (s, N−O str.); 715 (s, CF_3 def.). ^{1}H NMR (neat) δ: 4.90 (s, OCH_2O) ppm. ^{19}F NMR δ: +10.7 (t, 6F, $2CF_3N$, $J=12.4$ Hz); −34.0 (br, 4F, NCF_2CF_2N) ppm. MS *m/z*: 312 (17.5%, M$^+$); 293 [20.7, $(M-F)^+$]; 282 [27.5, $(M-CH_2O)^+$]; 243 [2.9, $(M-CF_3)^+$]; 182 (10.8, $C_3H_2F_6NO^+$); 164 (8.1, $C_3F_6N^+$); 150 (11.0, $C_2HF_5NO^+$); 149 (41.7, $C_2F_5NO^+$); 114 (35.7, $C_2F_4N^+$); 100 (9.6, $C_2F_4^+$); 94 (30.4, $C_2H_2F_2NO^+$); 69 (100.0, CF_3^+); 30 (36.3, CH_2O^+); 28 (24.9, CO^+).

(h) With 1,3-di-iodopropane

A mixture of mercurial **2** (1.73 g, 3.46 mmol) and 1,3-di-iodopropane (1.00 g, 3.38 mmol), was shaken at room temperature (24 h), but gave no volatile material. The residue was extracted with 1,1,2-trichlorotrifluoroethane (4×15 cm^3) and the solvent removed to give a dioxyl **1**/trimethylene copolymer **6** (0.93 g, *c.* 80%) [Analysis: Found: C, 24.0; H, 2.1%. Calc. for $(C_7H_6F_{10}N_2O_2)_n$: C, 24.7; H, 1.8%). IR $\nu_{max.}$ (cm^{-1}): 2920 (m, C−H str.); 1266–1170 (vs, C−F str.); 1047 (s, N−O str.); 706 (s, CF_3 def.). ^{1}H NMR ($CF_2ClCFCl_2$) δ: 4.18 (t, 4H, $2CH_2O$, $J=6.6$ Hz); 1.96 (quin., 2H, CH_2, $J=6.6$ Hz) ppm. ^{19}F NMR δ: +11.8 (t, 6F, $2CF_3N$, $J=10.7$ Hz); −25.9 (br., 4F, NCF_2CF_2N) ppm.

(i) With 1,2-dibromoethane

A mixture of mercurial **2** (2.16 g, 4.33 mmol) and 1,2-dibromoethane (1.33 g, 7.07 mmol), shaken at room temperature (17 d), gave unchanged dibromoethane (1.29 g, 6.86 mmol, 97% recovered) as the only volatile material.

(j) With dichlorodimethylsilane

A mixture of mercurial **2** (1.79 g, 3.59 mmol) and dichlorodimethylsilane (0.46 g, 3.59 mmol), shaken at room temperature (4 d), gave as the only volatile material 3,3,4,4-tetrafluoro-2,5-bis(trifluoromethyl)-7,7-dimethyl-1,6-dioxa-2,5-diaza-7-silacycloheptane (**7**) (nc) (1.19 g, 3.34 mmol, 93%) (Analysis: Found: C, 19.9; H, 1.8; F, 53.2; N, 8.0%; M$^+$, 356. $C_6H_6F_{10}N_2O_2Si$ requires: C, 20.2; H, 1.7; F, 53.4; N, 7.9%; M, 356), b.p. 135 °C; n_D^{20} 1.3280. IR $\nu_{max.}$ (cm^{-1}): 2967 and 2924 (w, C−H str.); 1271–1192 (vs, C−F str.); 1073, 1042 and 1030 (s, N−O and Si−O str.); 876 (s, Si−CH_3 str.); 705 (s, CF_3 def.). ^{1}H NMR (neat) δ: 0.48 (s, $SiMe_2$) ppm. ^{19}F NMR δ: +10.6 (t, 6F, $2CF_3N$, $J=13.0$ Hz); −36.2 (mult., 4F, NCF_2CF_2N) ppm. MS *m/z*: 356 (8.0%, M$^+$); 341 [4.7, $(M-CH_3)^+$]; 337 [5.0, $(M-F)^+$]; 257 [18.2, $(M-CF_3NO)^+$]; 142 (17.5, $C_2H_3F_3NOSi^+$); 114 (32.5, $C_2F_4N^+$); 81 (20.5, $C_2F_3^+$); 77 (100.0, $C_2H_6FSi^+$); 69 (71.3, CF_3^+); 47 (10.8, FSi^+).

(k) With 1,1-dichlorosilacyclobutane

A mixture of mercurial **2** (1.27 g, 2.55 mmol) and the silacyclobutane (0.35 g, 2.47 mmol), shaken at room temperature (5 d), gave as a volatile material (i) perfluoro-2-azapropene (0.03 g, 0.23 mmol, 9.5%), which condensed at −196 °C, and (ii) a 0 °C fraction, identified as 3,3,4,4-tetrafluoro-2,5-bis(trifluoromethyl)-1,6-dioxa-2,5-diaza-7-sila-7-spiro[3.6]decane (**8**) (nc) (0.58 g, 1.58 mmol, 64%) (Analysis: Found: C, 23.1; H, 1.8; F, 51.6; N, 7.9%. $C_7H_6F_{10}N_2O_2Si$ requires: C, 22.8; H, 1.6; F, 51.6; N, 7.6%), b.p. 161 °C; n_D^{20} 1.3521. IR $\nu_{max.}$ (cm^{-1}): 2950 and 2882 (w, C−H str.); 1266–1170 (vs, C−F str.); 1080, 1040 and 1030 (s, N−O and Si−O str.); 708 (s, CF_3 def.). ^{1}H NMR (neat) δ: 1.7 (br., $3CH_2$) ppm. ^{19}F NMR δ: +11.2 (t, 6F, $2CF_3N$, J = 13.6 Hz); −36.6 (mult., 4F, NCF_2CF_2N) ppm. MS *m/z*: 234 (1.1%, $C_5H_5F_5NOSi^+$); 133 (10.9, $C_2F_5N^+$); 123 (16.7, $C_2H_3F_2NOSi^+$); 114 (19.0, $C_2F_4N^+$); 108 (16.3, $C_3H_6F_2Si^+$); 92 (21.5, $C_2F_2NO^+$); 89 (4.0, $C_3H_6FSi^+$); 80 (30.2, $CH_2F_2Si^+$); 69 (100.0, CF_3^+); 47 (30.4, FSi^+); 44 (34.0, OSi^+); 42 (40.9, CH_2Si^+); 41 (27.5, $CHSi^+$); 39 (16.6, $C_3H_3^+$).

Reactions of perfluoro-2,5-diazahexane-2,5-diol (3)

(a) With trifluoroacetyl chloride in the presence of potassium fluoride

A mixture of diol **3** (0.83 g, 2.77 mmol), anhydrous potassium fluoride (1.0 g) and 1,1,1-trichlorotrifluoroethane (3 cm^3) was sealed *in vacuo* in a Rotaflo tube (*c.* 300 cm^3) and the tube shaken (0.5 h). The volatile material was removed *in vacuo* leaving a white solid (1.82 g) when trifluoroacetyl chloride (0.95 g, 7.17 mmol) was condensed *in vacuo* into the tube and the tube then shaken at room temperature (7 d). Fractional condensation *in vacuo* of the volatile products gave (i) trifluoroacetyl fluoride (0.23 g, 1.98 mmol, 27%) which condensed at −196 °C and (ii) a −23 °C fraction (0.97 g) which was shown (NMR spectroscopy) to consist of the unchanged diol **3** (0.215 g, 0.72 mmol, 25% recovered) and the diacetate **4d** (0.755 g, 1.54 mmol, 75%).

An experiment carried out in the absence of potassium fluoride using diol **3** (0.55 g, 1.83 mmol) and trifluoroacetyl chloride (0.53 g, 4.00 mmol) at room temperature (7 d) gave unchanged trifluoroacetyl chloride (0.51 g, 3.85 mmol, 96% recovered).

(b) With trifluoroacetyl chloride in the presence of quinoline

A mixture of diol **3** (0.59 g, 1.97 mmol) and quinoline (2 cm^3) was shaken *in vacuo* in a Rotaflo tube (*c.* 300 cm^3) to give a dark brown solution over a period of 5 min. Trifluoroacetyl chloride (1.07 g, 8.08 mmol) was then condensed *in vacuo* into the tube and the latter then shaken at room temperature (24 h). Fractional condensation *in vacuo* of the volatile material gave (i) unchanged trifluoroacetyl chloride (0.51 g, 3.85 mmol, 47.5% recovered) which condensed at −196 °C and (ii) a −23 °C fraction identified as the bis(trifluoroacetate) **4d** (0.84 g, 1.71 mmol, 87%).

(c) With dichlorodimethylsilane in the presence of quinoline

Dichloromethylsilane (0.205 g, 1.59 mmol) was condensed *in vacuo* into a Rotaflo tube (*c.* 300 cm^3) containing diol **3** (0.47 g, 1.57 mmol) and quinoline (2 cm^3), and the tube shaken at room temperature (24 h) to give the heterocycle **7** (0.40 g, 1.12 mmol, 71.5%) as the only volatile material.

(d) With iodoethane in the presence of quinoline

Iodoethane (0.48 g, 3.08 mmol) was condensed *in vacuo* into a Rotaflo tube (*c.* 300 cm^3) containing diol **3** (0.39 g, 1.30 mmol) and quinoline (2 cm^3), and the tube shaken at room temperature (24 h) to give unchanged iodoethane (0.085 g, 0.54 mmol, 17.5% recovered) as the only volatile material.

(e) With carbonyl chloride in the presence of quinoline

Carbonyl chloride (0.20 g, 2.02 mmol) was condensed *in vacuo* into a Rotaflo tube (*c.* 300 cm^3) containing diol **3** (0.55 g, 1.83 mmol) and quinoline (2 cm^3), and the tube shaken at room temperature (24 h) to give a volatile mixture (0.025 g, 0.50 mmol) of carbon dioxide, trifluoromethyl isocyanate and perfluoro-2-azapropene (IR spectroscopy).

Results and discussion

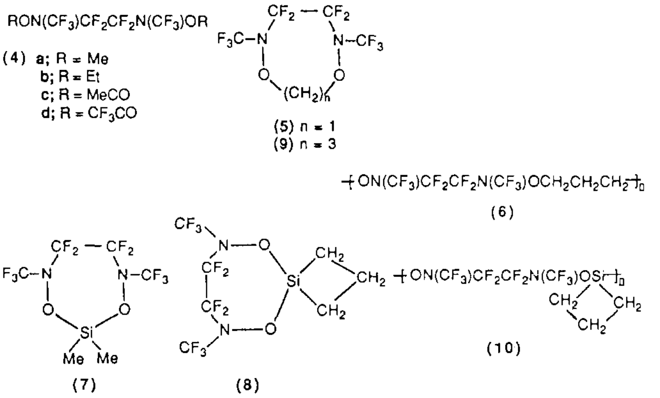
The results obtained from the reactions of mercurial **2** with halogen compounds *in vacuo* at room temperature (unless stated otherwise) are shown in Table 1.

Reactions involving the monoiodoalkanes and the acid chlorides were first carried out to determine whether the reactions occurred readily, as reported for the corresponding reactions of the mercurial $[(CF_3)_2NO]_2Hg$ [2], and if high yields of the disubstituted products **4** could be obtained.

TABLE 1. Reactions of mercurial **2**

Substrate	Molar ratio substrate/**2**	Time (d)	Substrate recovered (%)	Product (%)	
MeI	2.1:1	0.67	8.5	**4a**	89.5
MeBr	2.4:1	5	51.5	**4a**	91
EtI	1.4:1	0.83		**4b**	92.5
$CF_3CH_2I^a$	2.5:1	3	98.5		
MeCOCl	2.1:1	0.83	9	**4c**	87
CF_3COCl	2.5:1	7	30	**4d**	94.5
CH_2I_2	0.7:1	35		**5**	41.5
$I(CH_2)_3I$	1.0:1	1		**6**	80
$Br(CH_2)_2Br$	1.6:1	17	97		
Cl_2SiMe_2	1.0:1	4		**7**	93
$Cl_2\overline{SiCH_2CH_2CH_2}$	1.0:1	5		**8**	64

[a]At 50 °C.



In all of these reactions, except that with the iodide CF_3CH_2I, high yields of the products **4a–d** were obtained showing that both Hg–O bonds in the repeating unit of polymeric mercurial **2** were readily cleaved. The iodide CF_3CH_2I did not react with mercurial **2** even at 50 °C, presumably because of deactivation of the C–I bond by the strong $-I$ electron-withdrawing effect of the CF_3 group.

A major aim of the research was to determine if heterocyclic compounds could be made from halogenoalkanes and -silanes; dibromoalkanes were preferred to di-iodoalkanes because they are lower boiling and more stable, e.g. 1,2-di-iodoalkanes readily lose iodine to afford alkenes. First, the reactivity of a bromoalkane towards mercurial **2** relative to the reactivity of the corresponding iodoalkane was determined by the reaction of bromomethane with mercurial **2**. This was found to be considerably slower than that involving iodomethane, and after 5 d only a 53% conversion of **2** to product **4a** had taken place although the yield (91%) was high. It was therefore decided to investigate the reaction of 1,2-dibromoethane with **2** for an extended period (17 d) but, surprisingly, reaction did not take place and the alkane was recovered unchanged in high yield (97%). The reason for the lack of reactivity of the dibromide is not apparent, but the result indicates that only reaction with the more reactive and less stable di-iodoalkanes would be likely to be successful.

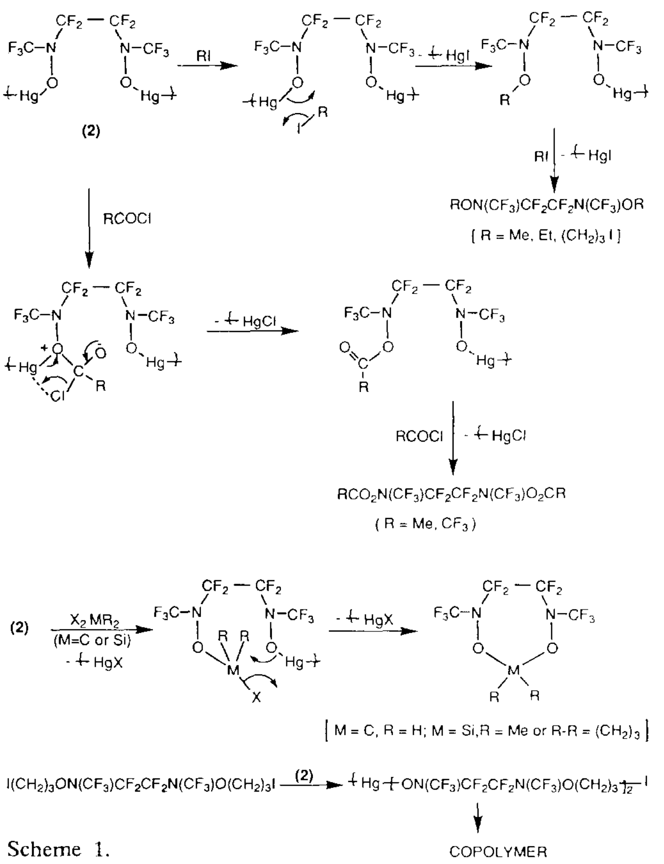
Reaction of di-iodomethane with **2** for an extended period (35 d), using an excess of the mercurial to try to ensure that both iodine atoms were replaced, gave a relatively low yield (41.5%) of the volatile seven-membered ring heterocycle **5**. The low yield could be due to incomplete reaction (CH_2I_2 is not volatile at 20 °C and if any had not reacted it would not have been recovered) or, more likely, to polymer formation as has been found to take place on reaction with phosgene [8]; the non-volatile residue was not examined because of the presence of an excess of **2**.

With 1,3-di-iodopropane, reaction gave a viscous 1:1 copolymer **6** in reasonable yield; cyclic compound **9** was not detected, thus, as expected, formation of the nine-membered heterocycle ring is much less favoured than formation of the seven-membered ring.

The mercurial $[(CF_3)_2NO]_2Hg$ reacts readily with silanes $Me_xSiCl_{(4-x)}$ ($x=0$, 2, 3) to give the corresponding O-silylhydroxylamines [2, 9], and with 1,1-dichloro-1-silacyclobutane to replace both chlorine atoms by the $(CF_3)_2NO$ group [10]. However, silyl derivatives of dioxyl **1** have not been reported.

Reaction of mercurial **2** with dichlorodimethylsilane resulted in the formation of the silicon-containing seven-membered ring heterocycle **7** in excellent yield (93%), while with 1,1-dichlorosilacyclobutane the novel spiro compound **8** was isolated in reasonable yield (64%). It is probable that the lower yield in the latter reaction was due to competing formation of polymer **10**.

The products can be explained by a concerted interaction via a cyclic transition state of an Hg–O bond in mercurial **2** with a C–halogen or Si–chlorine bond (Scheme 1). However, the observation that reaction of the mercurial $[(CF_3)_2NO]_2Hg$ with 1-iodo-2-methylpropane gave the compounds $(CF_3)_2NOH$ and $Me_2C{=}CH_2$,



Scheme 1.

as well as the expected product $Me_2CHCH_2ON(CF_3)_2$, could indicate that carbocation intermediates are involved in certain cases [11].

The results obtained show that mercurial **2** is a useful reagent for synthesising derivatives of dioxyl **1**, but it possesses several disadvantages, i.e. high toxicity, high moisture sensitivity, difficulty in handling and problems in preparation [three-fold excess of dioxyl **1** required for reasonable yield (60%–70%) in reasonable time (21 d) on a 5-mmol scale]. A more attractive precursor is diol **3** which has been isolated (83%) from the reaction of dioxyl **1** with hydrogen bromide at room temperature [6], but it readily sublimed *in vacuo* making separation from the bromine coproduct difficult. In the present work, the same preparative method was used except that the reaction was carried out in $CF_2ClCFCl_2$ solvent, and removal of bromine and solvent at 0 °C *in vacuo* left a near-quantitative yield of diol **3** in the reaction tube.

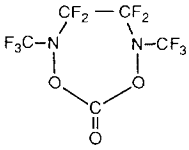
Reaction did not take place between diol **3** and trifluoroacetyl chloride at 20 °C (7 d), a lack of reactivity which is comparable to that of the hydroxylamine $(CF_3)_2NOH$. However, complexation of the hydroxylamine with an inorganic fluoride (KF or CsF) increased its nucleophilic reactivity so that it underwent reaction with acid chlorides, allyl halides and a range of inorganic halides [2]. The hydroxylamine also forms weakly-associated adducts with various amines [12].

The reaction of diol **3** with trifluoroacetyl chloride was re-investigated in the presence of potassium fluoride and reactions were also carried out between **3** and the halides CF_3COCl, Me_2SiCl_2, EtI and $COCl_2$ in the presence of quinoline. The results obtained are summarised in Table 2.

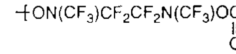
The reaction of trifluoroacetyl chloride with the diol **3**/KF complex [preformed from treatment of **3** with anhydrous KF in $CF_2ClCFCl_2$ solvent (0.5 h) followed by removal of the solvent] resulted in some fluorination of the acid chloride and formation of the desired ester **4d** in reasonable yield. However, the ester was contaminated with unreacted diol **3** which made purification necessary. An alternative procedure using an organic amine in place of the potassium fluoride was investigated. Quinoline was chosen as the amine because of its high boiling point (236 °C), so that possible contamination of the products with any free amine remaining at the end of the reaction would not be a problem.

Diol **3** was dissolved in quinoline *in vacuo* to give a colourless solution which rapidly darkened even in the absence of light, so the electrophilic reagent was introduced into the reaction tube immediately after the diol had dissolved (*c*. 5 min). Reaction with the halides CF_3COCl and Me_2SiCl_2 was eminently successful and gave the desired products **4d** and **7**, respectively, in good yield. However, with iodoethane, the expected volatile product **4b** was not formed; the dark green solid present in the tube was possibly 1-ethylquinolium iodide and diol **3**, or its quinoline complex was too weak a nucleophile to attack the salt at carbon with release of the base and formation of **4b**.

It was hoped that the reaction of the quinoline complex of diol **3** with phosgene would give heterocycle **11**, but the only volatile material obtained was a small amount of a mixture of carbon dioxide and breakdown products of the diol (CF_3NCO and $CF_3N{=}CF_2$). The probable outcome of the reaction was formation of a copolymer of dioxyl **1** and carbon monoxide, i.e. **12**, together with quinolinium chloride. Polymer **12** has been reported to be produced from reaction of dioxyl **1** with carbon monoxide [8] and reaction of mercurial **2** with phosgene [8].



(11)



$-\!\!\left[ON(CF_3)CF_2CF_2N(CF_3)O\underset{\underset{O}{\|}}{C}\right]_n$

(12)

The results obtained indicate that the complex formed between diol **3** and quinoline is only suitable for reaction

TABLE 2. Reactions of diol **3** with halides

Substrate	Molar ratio substrate/**3**	Complexing agent	Time (d)	Substrate recovered (%)	Products (%)	
CF_3COCl^a	2.2:1	–	7	96	**4d**	75^b
CF_3COCl	2.6:1	KF	7		CF_3COF	27
CF_3COCl	4.1:1	quinoline	1	47.5	**4d**	87
Me_2SiCl_2	1.0:1	quinoline	1		**7**	71.5
EtI	2.4:1	quinoline	1	17.5		–
$COCl_2^c$	1.1:1	quinoline	1			–

[a] In $CF_2ClCFCl_2$.

[b] Diol **3** (25% recovered) also obtained.

[c] A small amount of a volatile mixture of the compounds CO_2, CF_3NCO and $CF_3{=}CF_2$ was formed.

with active halides such as acid chlorides and chlorosilanes.

Acknowledgement

We thank Professor R.N. Haszeldine for his interest in this work.

References

1 R.E. Banks, R.N. Haszeldine and D.L. Hyde, *Chem. Commun.*, (1967) 413.

2 H.J. Emeléus and P.M. Spaziante, *Chem. Commun.*, (1968) 770; H.J. Emeléus, J.M. Shreeve and P.M. Spaziante, *J. Chem. Soc. A*, (1969) 431.

3 L.L. Nash, D.P. Babb, J.J. Couville and J.M. Shreeve, *J. Inorg. Nucl. Chem.*, *30* (1968) 3375; D.P. Babb and J.M. Shreeve, *Inorg. Chem.*, *6* (1967) 351; J.A. Lott, D.P. Babb, K.E. Pullen and J.M. Shreeve, *Inorg. Chem.*, *7* (1968) 2593.

4 A. Arfaei and S. Smith, *J. Chem. Soc., Perkin Trans. 1*, (1984) 1791.

5 R.E. Banks, K.C. Eapen, R.N. Haszeldine, P. Mitra, T. Myerscough and S. Smith, *J. Chem. Soc., Chem. Commun.*, (1972) 833.

6 R.E. Banks, K.C. Eapen, R.N. Haszeldine, A.V. Holt, T. Myerscough and S. Smith, *J. Chem. Soc., Perkin Trans. 1*, (1974) 2532.

7 M.J. Green and A.E. Tipping, unpublished results; M.J. Green, *Ph.D. Thesis*, University of Manchester, 1977.

8 M.T. Kanjia, S. Smith and A. Arfaei, unpublished results; M.T. Kanjia, *Ph.D. Thesis*, University of Manchester, 1977.

9 R.N. Haszeldine, D.J. Rodgers and A.E. Tipping, *J. Chem. Soc., Dalton Trans.*, (1975) 2225.

10 G.J. Ducker and A.E. Tipping, unpublished results; G.J. Ducker, *Ph.D. Thesis*, University of Manchester, 1976.

11 R.E. Banks and B. Justin, unpublished results; B. Justin, *Ph.D. Thesis*, University of Manchester, 1969

12 G.G. Flaskerud and J.M. Shreeve, *Inorg. Chem.*, *8* (1969) 2065.

13 M.T. Burke, R. Damrauer, R.A. Davies, G.T. Goodman and R.A. Karn, *J. Organometal. Chem.*, *43* (1972) 121.