Fluorocarbon Derivatives of Nitrogen. Part 5.[1] Replacement of Imidoyl Halogen by the Bistrifluoromethylamino-oxy Group: Reactions of Perfluoro-2-azapropene and Related Compounds with Bis(bistrifluoromethylamino-oxy)mercury(II) or *NN*-Bistrifluoromethylhydroxylamine–Caesium Fluoride [2]

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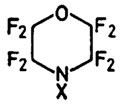
Treatment of perfluoro-2-azapropene with bis(bistrifluoromethylamino-oxy)mercury(II) yields the new mercurial $\{[(CF_3)_2NOCF_2](CF_3)N\}_2Hg$ (11), chlorinolysis of which provides the *N*-chloroamine $CF_3NClCF_2ON(CF_3)_2$ (16); pyrolysis of the mercurial (11) gives a complex mixture containing the imine $CF_3N{=}CFON(CF_3)_2$ (12) and material tentatively identified as $\{CF_3N{=}C[ON(CF_3)_2]\}_2O$. The *N*-chloro-compound (16) reacts with hydrogen chloride and silver cyanide to provide the corresponding amine $CF_3NHCF_2ON(CF_3)_2$ and the related imine (12). The latter product, together with the di-substituted analogue $(CF_3)_2NCF_2N{=}CFON(CF_3)_2$, can also be procured by treating perfluoro-2-azapropene with a caesium fluoride–*NN*-bistrifluoromethylhydroxylamine adduct. This reagent also attacks perfluoro-1-azacyclohexene to yield perfluoro-[2-(dimethylamino-oxy)-1-azacyclohexene] and perfluoro-[2,6-bis(dimethylamino-oxy)-1-azacyclohexene], and similarly effects nucleophilic substitution in pentafluoropyridine to provide 4-(bistrifluoromethylamino-oxy)-2,3,5,6-tetrafluoropyridine. The mercurial $[(CF_3)_2NO]_2Hg$ attacks the alkyliminocarbonyl chloride $Me_3CN{=}CCl_2$ to give the bistrifluoromethylamino-oxy-derivatives $Me_3CN{=}CCl[ON(CF_3)_2]$ and $Me_3CN{=}C[ON(CF_3)_2]_2$.

DURING an investigation centred on the synthesis of perfluoromorpholine *N*-oxyl (1),[3] an attempt to prepare the N–O–N compound (2) *via* treatment of perfluoro-*N*-nitromorpholine (3) with the mercurial (4) derived from the oxyl gave only perfluoro-[3-(morpholino-oxy)-5,6-dihydro-2*H*-1,4-oxazine] (5).[4] This unexpected result led to the discovery [4] that perfluoro-5,6-dihydro-2*H*-1,4-oxazine (6), presumed to be formed initially in the above reaction by denitrofluorination of the nitromorpholine, combines with the mercurial (4) to provide its derivative (5) in 88% yield at room temperature.† Subsequently,[5,6] the carbon analogue of (6), perfluoro-1-azacyclohexene (7) was shown to react with bis(bistrifluoromethylamino-oxy)mercury(II), $[(CF_3)_2NO]_2Hg$ (8), at room temperature to give perfluoro-[2-(dimethylamino-oxy)-1-azacyclohexene] (9) in 59% yield. To test the hypothesis that such replacement of imidoyl fluorine by a substituent delivered *via* a mercurial such as (4) or (8) involves the formation of thermally unstable adducts of type (A) and/or (B) ($X = O, CF_2$; R_F = fluorocarbon group), work was undertaken on reactions between the mercurial $[(CF_3)_2NO]_2Hg$ and the imines (7) and $CF_3N{=}CF_2$ (10) at low temperature.[7] The results achieved with the cyclic imine (7) were inconclusive but, as described below, a mercurial corresponding to type (B) has been prepared from the azapropene (10) and characterized.

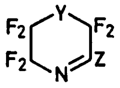


(1) $X = O^{\bullet}$

(2) $X = O\overline{NCF_2CF_2OCF_2CF_2}$

(3) $X = NO_2$

(4) $X = OHgO\overline{NCF_2CF_2OCF_2CF_2}$

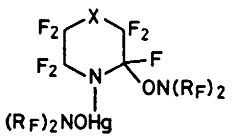


(5) $Y = O$; $Z = O\overline{NCF_2CF_2OCF_2CF_2}$

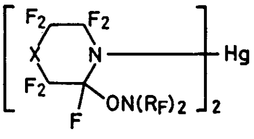
(6) $Y = O$; $Z = F$

(7) $Y = CF_2$; $Z = F$

(9) $Y = CF_2$; $Z = ON(CF_3)_2$



(A)



(B)

Preliminary experiments showed that bis(bistrifluoromethylamino-oxy)mercury(II) combines rapidly with a two-molar equivalent of perfluoro-2-azapropene at *ca.* 0 °C *in vacuo* to give a cream-coloured solid which, after a recovery procedure involving extraction with diethyl ether at room temperature under dry nitrogen, changed into a viscous yellow liquid. This oil, shown by ^{19}F n.m.r. spectroscopy to be an impure sample of the new mercurial $\{[(CF_3)_2NOCF_2](CF_3)N\}_2Hg$ (11), slowly evolved volatile material containing $CF_3N{=}CFON(CF_3)_2$ (12), $CF_3NHCF_2ON(CF_3)_2$ (13), and a compound thought to be $\{CF_3N{=}C[ON(CF_3)_2]\}_2O$ (14) when stored in an evacuated Pyrex ampoule at room temperature; at 100 °C complete decomposition occurred during 60 h, giving a complex mixture of volatile products which included compounds (12) (*ca.* 12% yield) and (14) (*ca.* 43%), the amine $(CF_3)_2NH$, and diethyl ether. A pure (according to ^{19}F n.m.r. spectroscopic analysis), pale-yellow, solid specimen of the mercurial (11) was isolated in 74% yield through the use of trichlorofluoromethane, both as a diluent in the $CF_3N{=}CF_2 + [(CF_3)_2NO]_2Hg$ reaction and as a solvent in the product work-up procedure. Storage at 40 °C for 75 min of a solution of this solid

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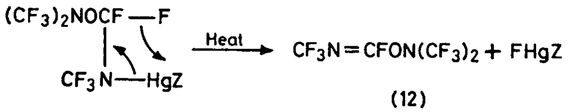
† The dihydro-oxazine (5) can also be prepared (46% yield) by treating the N–O–N compound (2) with triphenylphosphine in benzene at room temperature.[4]

mercurial in trichlorofluoromethane caused no apparent change in its ^{19}F n.m.r. spectrum; a neat sample of the mercurial melted at *ca.* 45 °C to a yellow liquid which decomposed completely when stored for 16 days at 100 °C in Pyrex in the absence of air, giving $CF_3N=CFON(CF_3)_2$ (12) (10% yield), $\{CF_3N=C[ON(CF_3)_2]\}_2O$ (14) (59%), small amounts of $(CF_3)_2NH$, CF_3NCO, $CF_3N=CF_2$, $(CF_3)_2NO\cdot$, $[(CF_3)_2N]_2Hg$, $CF_3N=C[ON(CF_3)_2]_2$ (15) and SiF_4, and a yellow solid containing Hg^+ and F^- ions.



(12)

Stage (i), Z = $N(CF_3)CF_2ON(CF_3)_2$
Stage (ii), Z = F

SCHEME 1

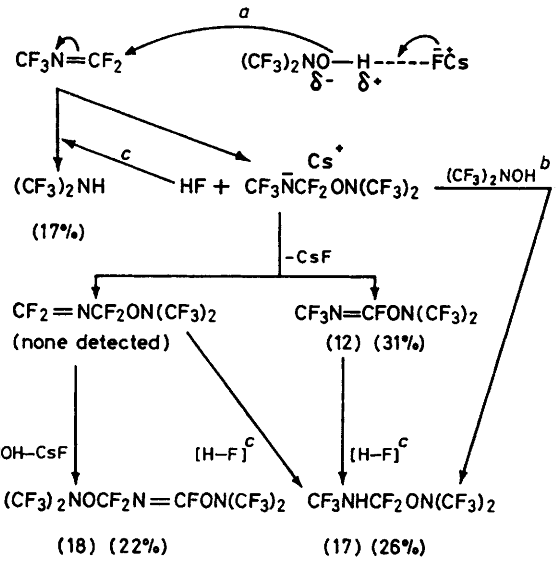
Formation of perfluoro-[1-(dimethylamino-oxy)-2-azapropene] (12) *via* pyrolysis of the mercurial $\{[(CF_3)_2NOCF_2](CF_3)N\}_2Hg$ (11) seems best visualised as shown in Scheme 1, which is adapted from mechanisms written previously [4,6] to account for the production of cyclic analogues of (12) *via* the routes (6) + (4) ⟶ (5) [4] and (7) + (8) ⟶ (9) [5] {*cf.* also $[(CF_3)_2N]_2Hg \longrightarrow$ (at 135 °C [8]) $CF_3N=CF_2 + HgF_2$}; that mercury(II) fluoride is released finds support in the detection amongst the products of the mercurial $[(CF_3)_2N]_2Hg$, the co-reactant perfluoro-2-azapropene {also found in the product mixture together with derivatives [$(CF_3)_2NH$, CF_3NCO] ascribable to its adventitious hydrolysis or reaction with glass [9]} required for its production presumably arising *via* dissociation of the starting material (11), a fragmentation which would lead to release of bistrifluoromethyl nitroxide (found amongst the products) and mercury: $\{[(CF_3)_2NOCF_2](CF_3)N\}_2Hg \longrightarrow CF_3N=CF_2 + [(CF_3)_2NO]_2Hg \longrightarrow$ (at 85 °C [10]) $2(CF_3)_2NO\cdot + Hg$. Discussion here of the speculative multi-stage mechanisms required [7] to account for the major pyrolysis product, $\{CF_3N=C[ON(CF_3)_2]\}_2O$ (14), cannot be justified on the basis of a single (and seemingly over-lengthy) pyrolysis experiment and the uncertainty surrounding the structure, which is tentatively assigned mainly on the basis of spectroscopic data that resemble, but are clearly different from those recorded [11] for the analogue $\{CF_3N=C[ON(CF_3)_2]\}_2$ [obtained *via* attack on trifluoromethyl isocyanide by bistrifluoromethyl nitroxide *].

$$(11) \xrightarrow[20\,°C]{Cl_2} \underset{(16)}{CF_3NClCF_2ON(CF_3)_2}\ (84\%) \xrightarrow[<20\,°C]{HCl} \underset{(17)}{CF_3NHCF_2ON(CF_3)_2}\ (96\%) \qquad (1)$$

Chemical proof of structure for the mercurial $\{[(CF_3)_2NOCF_2](CF_3)N\}_2Hg$ (11) was provided by the sequence (1). The amine (17) appeared as a by-product in a reaction between the *N*-chloro-compound (16) and silver cyanide at room temperature, presumably owing to failure to remove all moisture from the system [*cf.*[12] $(CF_3)_2NCl + H_2O \longrightarrow (CF_3)_2NH + CF_3N=CF_2$]; other products of this reaction were cyanogen chloride and the imine $CF_3N=CFON(CF_3)_2$ (12) (54%), as expected [*cf.*[13] $(CF_3)_2NBr + AgCN \longrightarrow CF_3N=CF_2 + BrCN + AgF$].

An authentic sample of the imine $CF_3N=CFON(CF_3)_2$ (12) was procured *via* nucleophilic attack on perfluoro-2-azapropene by the solid adduct *NN*-bistrifluoromethylhydroxylamine forms with anhydrous caesium fluoride; [14] this reaction leads also to the formation of the secondary amines $CF_3NHCF_2ON(CF_3)_2$ (17) and $(CF_3)_2NH$, plus the disubstituted product $(CF_3)_2NOCF_2N=CFON(CF_3)_2$ (18) (see Scheme 2).

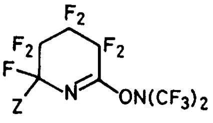
*Reactions involving Perfluoro-*1*-azacyclohexene, Pentafluoropyridine, and* 1,1*-Dichloro-*3,3*-dimethyl-*2*-azabut-*1*-ene.*—In keeping with the result of the reaction between perfluoro-2-azapropene and *NN*-bistrifluoromethylhydroxylamine in the presence of anhydrous caesium fluoride (Scheme 2), treatment of perfluoro-1-azacyclohexene with the hydroxylamine in the presence of an excess of the alkali-metal halide gave perfluoro-[2-(dimethylamino-oxy)-1-azacyclohexene] (9) and perfluoro-[2,6-bis(dimethylamino-oxy)-1-azacyclohexene] (19)≡(18) in 41 and 29% yield, respectively. These derivatives had been obtained less conveniently previously by



SCHEME 2 *Reagents and conditions:* [a] A reagent of composition $[(CF_3)_2NOH]_{2.5}\cdot CsF$ was employed, the molar ratio $(CF_3)_2NOH : CF_3N=CF_2$ being virtually 1 : 1. [b] If this step occurs, the salt $(CF_3)_2NO^-Cs^+$ also produced will act as a bistrifluoromethylamino-oxylating agent towards $CF_3N=CF_2$ and $CF_2=NCF_2ON(CF_3)_2$. [c] HF additions are presumably fluoride-initiated and involve $CsF\cdot HF$; $(CF_3)_2NOH$ may also act as a proton donor towards the nitranions implicated (*cf.* footnote *b*).

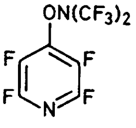
* The reaction [11] between CF_3NC and $(CF_3)_2NO\cdot$ also yields $CF_3N=C[ON(CF_3)_2]_2$, which was detected [product (15)] amongst the compounds produced by pyrolysis of the mercurial (11).

treating perfluoro-1-azacyclohexene with bis(bistrifluoromethylamino-oxy)mercury(II) [$\longrightarrow$ (9) (59%) + (19) (6%)] or (bistrifluoromethylamino-oxy)sodium;[5] the latter reagent gave (apparently) only the monosubstituted compound (9) in low yield (21%) owing to poor conversion (30%) of the substrate.* The adduct



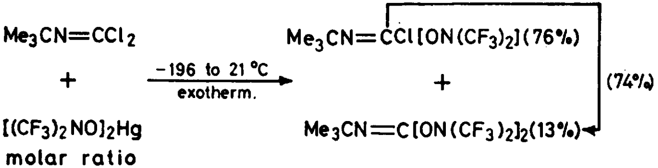
(9) Z = F

(19) Z = ON(CF$_3$)$_2$



(20)

[(CF$_3$)$_2$NOH]$_2$·CsF also proved more convenient than the salt Na$^+\bar{\text{O}}$N(CF$_3$)$_2$ [15] for the conversion of pentafluoropyridine into 4-(bistrifluoromethylamino-oxy)tetrafluoropyridine (20) [84% (isolated) yield based on 57% conversion of C_5F_5N at 50 °C].



(21)

SCHEME 3

In the hydrocarbon field, the [(CF$_3$)$_2$NO]$_2$Hg-imidoyl halide reaction has been employed to procure an authentic sample of 1,1-bis(bistrifluoromethylamino-oxy)-3,3-dimethyl-2-azabut-1-ene (21), required in connection with an investigation of attack by bistrifluoromethyl nitroxide on isocyanides[11] (see Scheme 3). Work on heterocyclic substrates is in progress.[17]

EXPERIMENTAL

Spectroscopic Analyses.—I.r. and n.m.r. (chemical shifts to *high* field of references designated *negative*) spectroscopy and mass spectrometry, respectively, were carried out with a Perkin-Elmer spectrophotometer model 257, a Perkin-Elmer R10 instrument (^{19}F at 56.46 and ^{1}H at 60 MHz), and an A.E.I. MS902 spectrometer (electron beam energy 70 eV). ^{19}F N.m.r. chemical shifts were measured relative to external trifluoroacetic acid.

Starting Materials.—Trifluoronitrosomethane, prepared from commercial trifluoroacetic acid,[18] was converted into perfluoro-2-azapropene,[9] *NN*-bistrifluoromethylhydroxylamine,[5] and bistrifluoromethyl nitroxide[5] by methods described in the literature. Bis(bistrifluoromethylamino-oxy)mercury(II) was produced as required from bistrifluoromethyl nitroxide and mercury †,[10] using a Pyrex reaction vessel in which the reaction under investigation was subsequently carried out. Perfluoro-1-azacyclohexene,[19] pentafluoropyridine,[20] and 1,1-dichloro-3,3-dimethyl-2-azabut-1-ene,[21] were prepared according to published procedures.

Reaction of Perfluoro-2-azapropene with Bis(bistrifluoromethylamino-oxy)mercury(II).—Perfluoro-2-azapropene (0.801 g, 6.02 mmol) and trichlorofluoromethane (0.51 g) (as an inert solvent) were condensed separately onto bis(bistrifluoromethylamino-oxy)mercury(II) (1.50 g, 2.77 mmol) contained in a cold (−196 °C), evacuated, Pyrex ampoule (20 cm^3) equipped with a Fischer-Porter PTFE needle valve (4 mm). The ampoule was sealed, allowed to warm to *ca.* 0 °C and then immersed in an ice-bath; after 30 min, it was shaken mechanically at room temperature for 1 h. Removal of the volatile product [shown by standard techniques to comprise CFCl$_3$ (0.51 g), CF$_3$N=CF$_2$ (0.25 g, 1.88 mmol, 31% recovery), CF$_3$NCO and COF$_2$ (traces of each)], *in vacuo*, left a yellowish solid residue which was washed out of the reaction vessel with trichlorofluoromethane; the washings were filtered through sintered glass under nitrogen to remove insoluble material, and the filtrate was evaporated under reduced pressure to give *bis-*[1-(*bistrifluoromethylamino-oxy*)-1,1,3,3,3-*pentafluoro-*2-*azaprop-*2-*yl*]*mercury* {1.65 g, 2.06 mmol, 74% based on [(CF$_3$)$_2$NO]$_2$Hg used} (Found: C, 12.2; N, 7.1. $C_8F_{22}HgN_4O_2$ requires C, 12.0; N, 7.0%), δ_F [*ca.* 30% w/v soln. in CFCl$_3$ (the solution was filtered under nitrogen to remove traces of insoluble material)] +30.2 {CF_3NHg, t, J_{CF_3,CF_2} 9.5 Hz [with distinct ^{199}Hg satellites (dt, $^3J_{Hg,CF_3}$ 73.3 Hz)]}, +19.4 (CF$_3$NHgCF_2, complex m), and +9.8 [(CF_3)$_2$NO, t, J_{CF_3,CF_2} 7.6 Hz] p.p.m. (rel. int. 3 : 2 : 6) {*cf.*[22] [(CF$_3$)$_2$N]$_2$Hg, δ_F (84.6 MHz; neat liq.) +29.3 p.p.m. ($^3J_{^{199}Hg,F}$ 72.8 Hz)}.

Reactions of Bis-[1-(*bistrifluoromethylamino-oxy*)-1,1,3,3,3-*pentafluoro-*2-*azaprop-*2-*yl*]*mercury* (11).—(a) *Chlorinolysis.* A sample of the mercurial (2.85 g, 3.55 mmol) was prepared in a Pyrex ampoule (80 cm^3) by treating perfluoro-2-azapropene with bis(bistrifluoromethylamino-oxy)mercury(II) (as described above) then pumping away volatile material. The ampoule was cooled to −196 °C, charged with chlorine (2.21 g, 31.3 mmol; dried with conc. H$_2$SO$_4$), and trichlorofluoromethane (0.67 g; as inert solvent), sealed *in vacuo*, allowed to warm to room temperature, and, finally, shaken mechanically for 18 h. Trap-to-trap fractional condensation of the volatile product, *in vacuo*, gave *perfluoro-*(2-*chloro-*5-*methyl-*4-*oxa-*2,5-*diazahexane*) (16) (2.01 g, 5.97 mmol, 84%; collected at −78 and −45 °C) [Found: C, 14.6; N, 8.6%; *M* (Regnault), 340. $C_4ClF_{11}N_2O$ requires C, 14.3; N, 8.3%; *M*, 336.5], δ_F (neat liq.) +13.9 (CF_3NCl; m), +8.8 [(CF_3)$_2$NO; m], and +6.6 p.p.m. (CF$_3$NClCF_2; br. m) (rel. int. 3 : 6 : 2), and *m/e* 263 [$C_4F_9N_2O^+$ (top mass peak); 7%], 175 ($C_3F_5N_2O^+$; 11%), 114 ($C_2F_4N^+$; 50%), and 69 (CF_3^+; 100%).

(b) *Thermolysis.* Using glove-box techniques (N$_2$ atmosphere), a sample of the mercurial (prepared as described above) was dissolved in 1,1,2-trichlorotrifluoroethane; the solution was filtered (sintered glass disc) to remove traces of a yellow solid and the filtrate was evaporated under reduced pressure. The white residue (4.87 g, 6.06 mmol) was heated (oil-bath) *in vacuo* in a small Pyrex ampoule (10 cm^3); it melted at *ca.* 45 °C, giving a yellowish liquid. After a while, when formation of a yellow solid was observed to com-

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* The low conversion can be ascribed to the unreliability of the method[15] employed to produce the sodium salt [(CF$_3$)$_2$NOH + Na]; a better method, developed more recently, involves treatment of the parent hydroxylamine with sodium hydride in ether or THF.[16]

† It is essential to use at least a three-fold (five-fold is preferred[10]) excess of *liquid* (CF$_3$)$_2$NO· to obtain material of composition [(CF$_3$)$_2$NO]$_x$Hg, where $x = 2$; with only a two-fold excess, the maximum value of x (determined by measurement of recovered nitroxide) we have achieved is *ca.* 1.6. Reinhard and Blackley (U.S.P. 3,644,449/1972) have defined conditions for the preparation of (bistrifluoromethylamino-oxy)mercury(I) ($x = 1$).

mence, the bath temperature was raised to 100 °C and maintained at that value for 16 days. Trap-to-trap fractional condensation *in vacuo* of the volatile product gave [fractions were examined by i.r., g.l.c., and *M* determination (Regnault) techniques]: (i) (−196 °C trap) a mixture (0.28 g, 1.93 mmol) of $(CF_3)_2NO\cdot$, $(CF_3)_2NH$, CF_3NCO, $CF_3N{=}CF_2$, SiF_4, and an unidentified component; (ii) (−96 °C trap) $CF_3N{=}CFON(CF_3)_2$ (0.06 g, 0.21 mmol) contaminated with a trace of $(CF_3)_2NH$; (iii) (−78 °C trap) $CF_3N{=}CFON(CF_3)_2$ (0.10 g, 0.35 mmol), $[(CF_3)_2NOC({=}NCF_3)]_2O$ (0.52 g, 0.96 mmol), and a trace of $(CF_3)_2NH$; (iv) (−45 °C trap) $[(CF_3)_2NOC({=}NCF_3)]_2O$ (14), $CF_3N{=}C[ON(CF_3)_2]_2$,[11] and a trace of $CF_3N{=}CFON(CF_3)_2$; and (v) (−24 °C trap) a colourless multi-component [by g.l.c. (3 m TXP-Celite, 70 °C); 2 major and several minor ' peaks '] liquid, which reacted with air with formation of a yellow solid and which was shown by ^{19}F n.m.r. analysis to contain the mercurial $[(CF_3)_2N]_2Hg$ and unidentified material carrying $(CF_3)_2NO$ groups. A sample of *perfluoro*-[3,5-*bis*(*dimethylamino-oxy*)-4-*oxa*-2,6-*diazahepta*-2,5-*diene*] (14) (1.41 g, 2.60 mmol) (Found: C, 17.2; N, 9.8. $C_8F_{18}N_4O_3$ requires C, 17.7; N, 10.3%) was isolated from the −45 °C trap fraction by g.l.c. (6 m TXP-Celite, 30 °C), $\lambda_{max.}$ 5.68 μm (C=N str.), δ_F (neat liq.) +21.0 (CF_3N; s) and +7.8 p.p.m. [$(CF_3)_2NO$; s] (rel. int. 1 : 2), and *m/e* 412 (unassigned top-mass peak; 24%), 263 $\{M^{\cdot+} - CF_3N{=}C[ON(CF_3)_2]O\cdot \longrightarrow {}^+C[ON(CF_3)_2]{=}NCF_3$; 30%}, 111 $\{{}^+C[ON(CF_3)_2]{=}NCF_3 - (CF_3)_2N\cdot \longrightarrow CF_3NCO^{\cdot+}$; 32%}, and 69 ($CF_3^+$; 100%). A yellow solid recovered from the reaction vessel responded positively in conventional qualitative tests for Hg^+ and F^- ions.

Reactions of Perfluoro-(2-*chloro*-5-*methyl*-4-*oxa*-2,5-*diazahexane*) (16).—(a) *With hydrogen chloride*. The *N*-chloro-compound (1.48 g, 4.40 mmol) and hydrogen chloride (0.292 g, 7.94 mmol) were condensed separately into a cold (−196 °C) evacuated Pyrex ampoule (20 cm³) equipped with a Rotaflo PTFE valve. The valve was closed, and the ampoule was taken out of the cooling bath to warm up; a reaction commenced before the ampoule and its contents attained room temperature, as revealed by the colour change caused by the generation of chlorine. After the ampoule had been shaken mechanically at room temperature for 3 h, the volatile product was fractionated, *in vacuo*, to provide a mixture (−196 °C trap) of chlorine and hydrogen chloride (0.153 g, 4.19 mmol, 53% recovery; determined after removal of the chlorine with mercury) and 2H-*octafluoro*-5-*trifluoromethyl*-4-*oxa*-2,5-*diazahexane* (17) (1.27 g, 4.20 mmol; 96% collected in − 78 and −45 °C traps) [Found: C, 16.2; H, 0.5; N, 9.5%; *M* (Regnault), 302. $C_4HF_{11}N_2O$ requires C, 15.9; H, 0.3; N, 9.3%; *M*, 302], $\lambda_{max.}$ 2.88m and 6.67s μm (N–H str. and bend, respectively), δ_F (*ca.* 50% soln. in $CFCl_3$) +20.7 (CF_3NH, br m), +10.7 (CF_3NHCF_2, br m), and +9.1 p.p.m. [$(CF_3)_2NO$, m] (rel. int. 3 : 2 : 6), δ_H (same soln.; 60 MHz; ext. C_6H_6 ref.) −2.2 p.p.m. (br s), and *m/e* 262.986 ($C_4F_9N_2O^+$, top mass peak; 15%), 174.993 ($C_3F_5N_2O^+$, 27%), 134.004 ($C_2F_5NH^+$, 6%), 113.995 ($C_2F_4N^+$, 100%), and 110.992 (CF_3NCO^+, 16%).

(b) *With silver cyanide*. Silver cyanide (1.14 g, 8.51 mmol) was dried by heating it under dynamic vacuum at 125 °C for 4 h in a Pyrex ampoule (20 cm³); the ampoule was then cooled (−196 °C), charged with perfluoro-(2-chloro-5-methyl-4-oxa-2,5-diazahexane) (0.37 g, 1.09 mmol), sealed (Rotaflo PTFE valve), and shaken mechanically at room temperature for 19 h. Examination of the volatile product by i.r. spectroscopy revealed that little change had occurred, so the reaction mixture was transferred to a smaller evacuated Pyrex ampoule (10 cm³) and shaken at room temperature for 89 h. Work-up of the product by standard techniques revealed that it contained perfluoro-(2-chloro-5-methyl-4-oxa-2,5-diazahexane), cyanogen chloride, trifluoromethyl isocyanate, 2*H*-octafluoro-5-trifluoromethyl-4-oxa-2,5-diazahexane (17) (0.33 mmol, 30%), and perfluoro-[1-(dimethylamino-oxy)-2-azapropene] (12) (0.59 mmol, 54%). A grey solid left in the reaction vessel gave a positive test for fluoride ion.

Reactions of NN-*Bistrifluoromethylhydroxylamine–Caesium Fluoride*.—(a) *With perfluoro*-2-*azapropene*. *NN*-Bistrifluoromethylhydroxylamine (3.11 g, 18.5 mmol) was condensed into a cold (−196 °C) evacuated Pyrex ampoule (20 cm³) containing finely powdered caesium fluoride (0.90 g, 5.92 mmol) which had been dried (in the same ampoule) at 200 °C for 11 h under dynamic vacuum. The ampoule was sealed (4 mm Fischer-Porter PTFE needle valve) and vibrated mechanically at room temperature for 21 h. The excess of *NN*-bistrifluoromethylhydroxylamine (0.61 g, 3.63 mmol) was pumped out and replaced with perfluoro-2-azapropene (1.95 g, 14.7 mmol) after the ampoule had been re-cooled to −196 °C. The reaction mixture was then shaken for 2.3 h at room temperature. Analysis [i.r., g.l.c., and *M* determination (Regnault)] of fractions obtained by trap-to trap fractional condensation of the volatile product, *in vacuo*, showed it to contain the following compounds plus several ' unknowns ': $(CF_3)_2NH$ (2.55 mmol, 17%), $CF_3NHCF_2ON(CF_3)_2$ (3.87 mmol, 26%), $CF_3N{=}CFON(CF_3)_2$ [4.49 mmol, 31% (this condensed mainly in a −78 °C trap)], $(CF_3)_2NOCF_2N{=}CFON(CF_3)_2$ [3.25 mmol, 22% (condensed mainly at −45 °C)] (all yields are based on $CF_3N{=}CF_2$). Samples of the third {*perfluoro*-[1-(*dimethylamino-oxy*)-2-*azapropene*] (12) (1.09 g, 3.87 mmol, 26%) [Found: C, 17.3; N, 10.2%; *M* (Regnault), 276. $C_4F_{10}N_2O$ requires C, 17.0; N, 9.9%; *M*, 282], $\lambda_{max.}$ (vapour) 5.59s (C=N str.) and 9.36s μm (N–O str.), δ_F (neat liq.) +34.0 (N=C*F*, br, structureless), +20.2 (CF_3N, d, $J_{CF_3,CF}$ 11.5 Hz), and +7.5 p.p.m. [$(CF_3)_2NO$, s] (rel. int. 1 : 3 : 6), and *m/e* 263 ($M^{\cdot+} - F\cdot \longrightarrow C_4F_9N_2O^+$, 6%), 175 ($C_3F_5N_2O^+$, 10%), 114 ($C_2F_4N^+$, 45%), and 69 ($CF_3^+$, 100%)} and fourth {*perfluoro*-[1,3-*bis*(*dimethylamino-oxy*)-2-*azapropene*] (18) (Found: C, 16.9; N, 10.0. $C_6F_{10}N_3O_2$ requires C, 16.7; N, 9.7%), $\lambda_{max.}$ (vapour) 5.61s (C=N str.), 9.41s and 9.58m μm (N–O str.), δ_F (neat liq.) +35.6 (N=C*F*, br s), +13.0 (CF_2N, m), +8.2 [$(CF_3)_2NOCF_2$, t, J_{CF_3,CF_2} 7 Hz], and +7.4 p.p.m. [$(CF_3)_2NOCF{=}N$, s] (rel. int. 1 : 2 : 6 : 6), and *m/e* 412 [$M^{\cdot+} - F\cdot \longrightarrow C_6F_{14}N_3O_2^+$ (top mass peak), 15%], 263 ($C_4F_9N_2O^+$, 45%), 175 ($C_3F_5N_2O^+$, 29%), 130 ($C_2F_4NO^+$, 38%), 114 ($C_2F_4N^+$, 33%), 111 ($C_2F_3NO^+$, 28%), 92 ($C_2F_2NO^+$, 38%), 69 (CF_3^+, 100%), and 47 (COF^+, 37%)} of these products were isolated by g.l.c. (6 m TXP-Celite. 25 °C).

(b) *With perfluoro*-1-*azacyclohexene*. *NN*-Bistrifluoromethylhydroxylamine (0.68 g, 4.02 mmol) was condensed, *in vacuo*, into a cold (−196 °C) evacuated Pyrex ampoule (20 cm³) containing an excess of anhydrous caesium fluoride (1.46 g, 9.60 mmol) (dried, *in situ*, at 180 °C for 8 h under dynamic vacuum). The ampoule was sealed (PTFE needle valve), shaken at room temperature for 2 h, cooled to −196 °C, and then charged with perfluoro-1-azacyclohexene [*ca.* 0.97 g, 4.0 mmol (contaminated with traces of benzene, the solvent used in its preparation [19])] before being re-sealed and shaken at room temperature for 3 h. Work-up of the volatile product by a combination of distillation and g.l.c. (3 m SE30, 60 °C) techniques afforded perfluoro-[2-(dimethylamino-oxy)-1-azacyclohexene] (0.65 g, 1.65 mmol, 41%; identified by comparison of its i.r. spectrum and g.l.c. retention time with that of an authentic specimen[5]) and perfluoro-[2,6-bis(dimethylamino-oxy)-1-azacyclohexene] (0.64 g, 1.18 mmol, 29%) (Found: C, 20.0; N, 7.9. Calc. for $C_9F_{19}N_3O_2$: C, 19.9; N, 7.7%), b.p. (Siwoloboff) 140 °C at 755 mmHg, the i.r. and ^{19}F n.m.r. spectra of which checked well with those of the sample isolated previously.[5]

(c) *With pentafluoropyridine.* Pentafluoropyridine (1.61 g, 9.53 mmol) was condensed, *in vacuo*, into a cold (−196 °C) Pyrex ampoule (20 cm³) containing preformed *NN*-bistrifluoromethylhydroxylamine–caesium fluoride adduct [from 1.61 g (9.53 mmol) of $(CF_3)_2NOH$ and 0.65 g (4.28 mmol) of anhydrous caesium fluoride]. The ampoule was sealed (PTFE needle valve) and shaken first at room temperature for 87 h then, since the reaction was proceeding only slowly (discovered through g.l.c. analysis of volatile material withdrawn from the reaction vessel), at 50 °C for 24 h. Work-up of the volatile product by a combination of distillation and g.l.c. (3 m SE30–Celite, 70 °C) techniques provided 4-(bistrifluoromethylamino-oxy)-2,3,5,6-tetrafluoropyridine (1.46 g, 4.59 mmol, 48%) [Found: C, 26.7; N, 8.8%; *M* (mass spec.), 318. Calc. for $C_7F_{10}N_2O$: C, 26.4; N, 8.8%; *M*, 318], b.p. (Siwoloboff) 131 °C at 740 mmHg, δ_F (neat liq.) +8.0 [$(CF_3)_2NO$; t, $J_{3(5)F,CF_3}$ 4 Hz], −12.5 (2-, 6-F; m), and −80.6 p.p.m. (3-, 5-F; m) (rel. int. 3 : 1 : 1). G.l.c. analysis of distillation fractions indicated that at least 4.08 mmol (43% recovery) of pentafluoropyridine remained unchanged; 2.54 mmol (27%) of *NN*-bistrifluoromethylhydroxylamine was present in the volatile product. The white solid residue left in the reaction vessel was not examined.

Reaction of Bis(bistrifluoromethylamino-oxy)mercury(II) *with* 1,1-*Dichloro*-3,3-*dimethyl*-2-*azabut*-1-*ene* (*with C. W. Stephens*).—The dichloro-compound (0.92 g, 5.97 mmol) was condensed, *in vacuo*, onto the mercurial (3.37 g, 6.27 mmol) contained in a cold (−196 °C) Pyrex ampoule (100 cm³). When the tube was left at room temperature to warm up, a slightly exothermic reaction occurred. Trap-to-trap fractional condensation of the volatile product at 1—2 mmHg provided three fractions: (*i*) (−23 °C trap) a mixture [analysed by coupled g.l.c.–i.r. (2 m SE30, 70 °C) and *M* (Regnault determination)] of 1,1-bis(bistrifluoromethylamino-oxy)-3,3-dimethyl-2-azabut-1-ene (0.18 g, 0.43 mmol) and 1-(*bistrifluoromethylamino-oxy*)-1-*chloro*-3,3-*dimethyl*-2-*azabut*-1-*ene*, a sample (0.58 g, 2.02 mmol) (Found: C, 29.3; H, 3.1. $C_7H_9ClF_6N_2O$ requires C, 29.3; H, 3.1%), b.p. 88—90 °C at 755 mmHg (Siwoloboff), $\lambda_{max.}$ (vapour) 5.70 μm (C=N str.), δ_F [neat liq.; 94.1 MHz, with *p*-$CF_3SC_6H_4Cl$ lock (35.5 p.p.m. to low field of CF_3CO_2H)] +9.1 (s) p.p.m., δ_H (100 MHz; TMS lock) +1.03 (s) p.p.m., and *m/e* 273 and 271 [$M^{+\cdot}$ (^{37}Cl) − $CH_3\cdot$, 14% and $M^{+\cdot}$ (^{35}Cl) − $CH_3\cdot$, 41%; top mass peaks], 84 ($C_4H_6NO^+$, 93%), 69 (CF_3^+, 76%), 57 ($C_4H_9^+$, 100%), 56 ($C_3H_6N^+$, 58%), and 41 (CH_3CN^+, 74%) [metastable peak observed at *m/e* 37.3, corresponding to $(CH_3)_2CN : C : O^+ (84) \longrightarrow (CH_3)_2CN^+ (56) + CO$], of which was isolated by preparative g.l.c.; (*ii*) (−46 °C) and (*iii*) (−78 °C), both mixtures of the two compounds in the −23 °C trap. The estimated yields of the two products were: $Me_3CN{:}CCl[ON(CF_3)_2]$ 4.51 mmol (76%), and $Me_3CN{:}C[ON(CF_3)_2]_2$ 0.76 mmol (13%); the latter was identified by comparison of its i.r. spectrum and g.l.c. retention time with that of an *authentic specimen* (0.52 g, 1.25 mmol, 74%) (Found: C, 25.5; H, 2.4. $C_9H_9F_{12}N_3O_2$ requires C, 25.8; H, 2.15%), b.p. 72—74 °C at 747 mmHg (Siwoloboff), $\lambda_{max.}$ (vapour) 5.65 μm (C=N str.), δ_F (neat liq., 94.1 MHz, *p*-$CF_3SC_6H_4Cl$ lock) +8.16 p.p.m. (s), δ_H (100 MHz; $SiMe_4$ lock) +0.92 (s) p.p.m., which was isolated by a combination of fractional condensation and g.l.c. (2 m SE30, 22 °C) from the volatile product obtained by allowing a mixture of the mercurial $[(CF_3)_2NO]_2Hg$ (0.92 mmol) and the monochloro-compound $Me_3CN{=}CCl[ON(CF_3)_2]$ (1.68 mmol) to warm from −196 °C to room temperature in the absence of air in a Pyrex ampoule (100 cm³).

We are indebted to the Government of Pakistan for the award of a Merit Scholarship to D. R. C., and to Professor R. N. Haszeldine F.R.S. for providing facilities.

[0/1505 *Received, 2nd October*, 1980]

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