

Nitroxide Chemistry. Part III.¹ Photolysis of Bistrifluoromethyl Nitroxide and Some Reactions of the Major Product, Perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane)²

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U.v. irradiation of bistrifluoromethyl nitroxide yields perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) together with oxygen, carbonyl fluoride, trifluoronitrosomethane, trifluoronitromethane, *O*-nitroso-*NN*-bistrifluoromethylhydroxylamine, and tristrifluoromethylhydroxylamine. Perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) decomposes thermally to bistrifluoromethyl nitroxide and tetrakis(trifluoromethyl)hydrazine and reacts (i) with hydrogen iodide to yield equimolar amounts of *NN*-bistrifluoromethylhydroxylamine and bistrifluoromethylamine, (ii) with nitric oxide to give equimolar amounts of *O*-nitroso-*NN*-bistrifluoromethylhydroxylamine and bistrifluoromethylnitrosamine, and (iii) with fluoro-olefins to yield 1:1 adducts of the type $(CF_3)_2N \cdot O \cdot CFX \cdot CFY \cdot N(CF_3)_2$ [for $CF_2 \cdot CF_2$, X = Y = F; for $CF_2 \cdot CFCl$, X = Cl, Y = F; for $CF_2 \cdot CF \cdot CF_3$, X = CF_3 , Y = F (major product) and X = F, Y = CF_3 (minor); for $CF_2 \cdot CHF$, X = F, Y = H (80%) and X = H, Y = F (20%)] and, in the cases of tetrafluoroethylene and chlorotrifluoroethylene, polymeric material.

ULTRAVIOLET irradiation of bistrifluoromethyl nitroxide is claimed to yield *O*-nitroso-*NN*-bistrifluoromethylhydroxylamine, tristrifluoromethylhydroxylamine, and the peroxidic dimer of the nitroxide, $(CF_3)_2N \cdot O \cdot O \cdot N(CF_3)_2$, b.p. 48–49°, identical with material obtained *via* treatment of the nitroxide with tin or with phosphorus trifluoride.³ The peroxide structure was assigned on the basis of elemental analysis, molecular weight determination (method unstated), the appearance of a mass spectral peak assignable to O_2^+ (no other data were quoted), the ability of the material to liberate 2 equiv. of iodine from acidified potassium iodide, and the dissociation of 'about half of the compound' into bistrifluoromethyl nitroxide when it was pyrolysed

¹ Part II, R. E. Banks, R. N. Haszeldine, and B. Justin, *J. Chem. Soc. (C)*, 1971, 2777.

² Presented, in part, at the 6th International Symposium on Fluorine Chemistry, Durham, 18–23 July, 1971.

³ S. P. Makarov, A. Ya. Yakubovich, S. S. Dubov, and A. N. Medvedev, *Zhur. vsesoyuz. khim. Obsch. im. D.I. Mendeleeva*, 1965, 106; S. P. Makarov, M. A. Énglin, A. F. Videiko, V. A. Tobolin, and S. S. Dubov, *Doklady Akad. Nauk S.S.S.R.*, 1966, **168**, 344; S. P. Makarov, A. F. Videiko, V. A. Tobolin, and M. A. Énglin, *Zhur. obsch. Khim.*, 1967, **37**, 1528.

at 180 °C with a contact time of 3–5 s. We find that the major organic product arising from photolysis of bistrifluoromethyl nitroxide is perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane), $(CF_3)_2N \cdot O \cdot N(CF_3)_2$, b.p. 48.5°,⁴ as suggested previously might be the case.⁵ The diazapentane is not a new compound, having been prepared previously by, for example, photolysis of tristrifluoromethylhydroxylamine⁴ and reaction of bistrifluoromethyl nitroxide with trifluoronitrosomethane.⁶

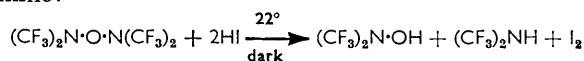
U.v. irradiation of bistrifluoromethyl nitroxide for 19 h gave oxygen [30% yield based on the stoichiometry $4(CF_3)_2N \cdot O \cdot \rightarrow 1O_2$], traces of silicon tetrafluoride, and the following organic products: $(CF_3)_2N \cdot O \cdot N(CF_3)_2$ (63%), $(CF_3)_2N \cdot O \cdot CF_3$ (10%), $(CF_3)_2N \cdot O \cdot NO$ (13%), $CF_3 \cdot NO_2$ (3%), COF_2 (2%), $CF_3 \cdot NO$ (trace), and $(CF_3)_2N \cdot O \cdot$ (trace); the same products were

⁴ R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc. (C)*, 1966, 1236.

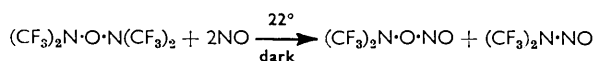
⁵ A. R. Forrester, J. M. Hay, and R. H. Thomson, 'Organic Chemistry of Stable Free Radicals,' Academic Press, London and New York, 1968, p. 200.

⁶ R. E. Banks, R. N. Haszeldine, and M. J. Stevenson, *J. Chem. Soc. (C)*, 1966, 901.

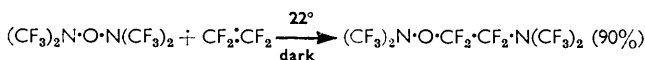
obtained when the irradiation period was approximately halved, but 30% of the nitroxide was recovered. The perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) was identical both spectroscopically and chemically with material prepared by the two routes^{4,6} already mentioned. Chemically, its structure was established through its thermal decomposition to give (within the limits of experimental error) the calculated mixture of bistrifluoromethyl nitroxide and the hydrazine $(\text{CF}_3)_2\text{N}\cdot\text{N}(\text{CF}_3)_2$ and by its reaction (i) with anhydrous hydrogen iodide to yield an equimolar mixture of *NN*-bistrifluoromethylhydroxylamine and bistrifluoromethylamine:



(ii) with nitric oxide to give *O*-nitroso-*NN*-bistrifluoromethylhydroxylamine and bistrifluoromethylnitrosamine:

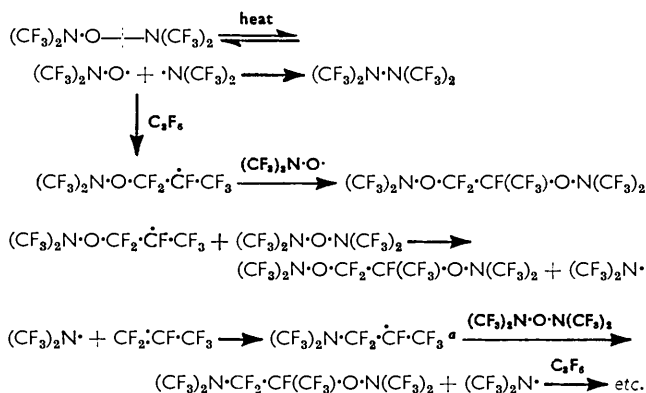


and (iii) with fluorinated olefins, *e.g.*



Reactions between perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) and tetrafluoroethylene, chlorotrifluoroethylene (telomeric material was also obtained from these olefins, and polytetrafluoroethylene in the case of the first), or trifluoroethylene proceed slowly at room temperature in the dark, and in the cases of the unsymmetrical ethylenes the $(\text{CF}_3)_2\text{N}$ group becomes attached preferentially to that carbon atom of the olefin known to be the more susceptible towards free-radical attack [$\text{CF}_2\cdot\text{CFCl} \rightarrow (\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{CFCl}\cdot\text{CF}_2\cdot\text{N}(\text{CF}_3)_2$ apparently exclusively; $\text{CF}_2\cdot\text{CHF} \rightarrow (\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{CF}_2\cdot\text{CHF}\cdot\text{N}(\text{CF}_3)_2$ (80%), $(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{CHF}\cdot\text{CF}_2\cdot\text{N}(\text{CF}_3)_2$ (20%)]. Perfluoropropene combines much more slowly with the diazapentane at room temperature than do the fluoroethylenes, and when reaction is forced at 85 °C a mixture of the adducts $(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{CF}(\text{CF}_3)\cdot\text{CF}_2\cdot\text{N}(\text{CF}_3)_2$ (*ca.* 80%) and $(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{CF}(\text{CF}_3)\cdot\text{CF}_2\cdot\text{O}\cdot\text{N}(\text{CF}_3)_2$ (*ca.* 20%) is obtained. The nature of the products from these addition reactions is indicative of a free-radical mechanism, and since the diazapentane undergoes N-O bond fission when heated [$\rightarrow (\text{CF}_3)_2\text{N}\cdot\text{O}\cdot + (\text{CF}_3)_2\text{N}\cdot \rightarrow (\text{CF}_3)_2\text{N}\cdot\text{N}(\text{CF}_3)_2$], and thus turns purple when kept at 85 °C, the reaction involving perfluoropropene seems easily explained (see Scheme); the absence of the adduct $(\text{CF}_3)_2\text{N}\cdot\text{CF}_2\cdot\text{CF}(\text{CF}_3)\cdot\text{N}(\text{CF}_3)_2$ can reasonably be ascribed to steric factors.* The room temperature reactions of perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) with the more reactive olefins (*cf.* ref. 7) tetrafluoroethylene, chlorotrifluoroethylene, and trifluoroethylene may, similarly, be initiated by attack of

$(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot$ or $(\text{CF}_3)_2\text{N}\cdot$ radical formed by slight dissociation of the diazapentane; however, the possibility also exists that they may be initiated by or proceed predominantly by a molecule-molecule interaction (this



SCHEME

* $(\text{CF}_3)_2\text{N}\cdot$ radical produced thermally or photochemically from the *N*-halogen-compounds $(\text{CF}_3)_2\text{N}\cdot\text{X}$ ($\text{X} = \text{Cl}$ or Br) attacks the terminal position in perfluoropropene almost exclusively (> 95%).⁷

also applies to the reaction between the diazapentane and nitric oxide), and this facet of the chemistry of perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) is receiving further attention.

EXPERIMENTAL

I.r. spectra were measured with a Perkin-Elmer spectrophotometer model 257, n.m.r. spectra with a Perkin-Elmer R10 instrument (¹⁹F at 56.46 MHz and ¹H at 60.00 MHz), and mass spectra with an A.E.I. MS902 spectrometer. Regnault's method was used to determine molecular weights unless stated otherwise. Conventional vacuum-line techniques were used to separate mixtures of volatile reaction products.

Photolysis of Bistrifluoromethyl Nitroxide.—The nitroxide (3.15 g, 18.8 mmol), sealed in a silica ampoule (200 ml), the lower end of which was wound with black tape to prevent irradiation of liquid product, was subjected to u.v. light from a Hanovia 250 W lamp placed 20 cm distant for 19 h. The gaseous purple radical was thus converted into a product composed of a pale yellow liquid surmounted by a pale blue gas. Work-up by standard techniques showed the product to contain oxygen (1.40 mmol), perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (6.22 mmol), tristrifluoromethylhydroxylamine (1.88 mmol), *O*-nitroso-*NN*-bistrifluoromethylhydroxylamine (2.53 mmol), trifluoronitromethane (0.55 mmol), carbonyl fluoride (0.30 mmol), traces of trifluoronitrosomethane, bistrifluoromethyl nitroxide, and silicon tetrafluoride, and a small amount of a colourless liquid which condensed in a -46 °C trap when the reaction product was fractionated *in vacuo* and decomposed with evolution of silicon tetrafluoride when the trap was allowed to warm to room temperature. Pure (by g.l.c.) perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (1.97 g, 6.16 mmol) (Found: C, 15.3; N, 8.5%; *M*, 322. Calc. for $\text{C}_4\text{F}_{12}\text{N}_2\text{O}$: C, 15.0; N, 8.75%; *M*,

⁷ R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc.*, 1965, 6141; G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc. (C)*, 1971, 3833.

* It is impossible to construct a Courtauld molecular model of this compound even by use of 'fluorines' with bevelled edges, whereas a model of the adduct $(\text{CF}_3)_2\text{N}\cdot\text{CF}_2\cdot\text{CF}(\text{CF}_3)\cdot\text{O}\cdot\text{N}(\text{CF}_3)_2$ can be made.

320) was isolated (-72°C trap) by simple trap-to-trap fractional condensation of the reaction product *in vacuo*; the i.r. spectrum of this material was identical with that of a sample prepared by photolysis of tristrifluoromethylhydroxylamine ⁴ and its ¹⁹F n.m.r. spectrum consisted of a singlet at -9.68 p.p.m. relative to $\text{CF}_3\cdot\text{CO}_2\text{H}$ (interchange ref.; lit.⁴ -10.0 p.p.m.).

The photolysis was repeated with 3.45 g (20.5 mmol) of bistrifluoromethyl nitroxide and a shorter irradiation period (8 h). The product contained oxygen (2.22 mmol), perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (5.45 mmol), tristrifluoromethylhydroxylamine (1.57 mmol), *O*-nitroso-*NN*-bistrifluoromethylhydroxylamine (0.60

fluoromethylhydrazine (0.082 g, 0.270 mmol), shown by i.r. spectroscopy to contain traces of *NN*-bistrifluoromethylhydroxylamine and unknown material, and (ii) (-140°C trap) a mixture of bistrifluoromethyl nitroxide (0.087 g, 0.518 mmol) and tetrakisbistrifluoromethylhydrazine (0.026 g, 0.086 mmol) {the composition was calculated by mixing the fraction with an excess of tetrafluoroethylene to convert the nitroxide into perfluoro-[1,2-bis(dimethylamino-oxy)ethane],⁶ which was easily isolated by trap-to-trap fractional condensation techniques}.

(b) *With hydrogen iodide.* Perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (0.224 g, 0.700 mmol) was condensed, *in vacuo*, into a cold (-196°C) Pyrex tube (50 ml) containing

TABLE 1

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

$(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{N}(\text{CF}_3)_2$ (g, mmol)	Olefin (g, mmol) $\text{CF}_2:\text{CF}_2$	Time (h)	Products (g, mmol, % yield)	Elemental analyses and molecular weights
0.777, 2.43	0.243, 2.43	24	$(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{N}(\text{CF}_3)_2$ ^{b,c} (0.756, 1.80, 74) $(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{N}(\text{CF}_3)_2$ (0.133, 0.417, 17) $(\text{CF}_3)_2\text{NH}$ (traces) $\text{CF}_2\cdot\text{CF}_2$ (traces)	Found: C, 17.4; N, 6.65%; <i>M</i> , 420 ^d Required: C, 17.15; N, 6.65%; <i>M</i> , 420
0.697, 2.18	$\text{CF}_2:\text{CFCl}$ 0.256, 2.20	240 ^e	$(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{CFCl}\cdot\text{CF}_2\cdot\text{N}(\text{CF}_3)_2$ ^e (0.895, 2.05, 93) $(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{N}(\text{CF}_3)_2$ (0.023, 0.073, 3)	Found: C, 16.5; N, 6.4%; <i>M</i> , 436.5 ^d Required: C, 16.5; N, 6.4%; <i>M</i> , 436.5
0.783, 2.45	$\text{CF}_2:\text{CF}\cdot\text{CF}_3$ 0.366, 2.44	13 ^f	$(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{CF}(\text{CF}_3)\cdot\text{CF}_2\cdot\text{N}(\text{CF}_3)_2$ (1) (0.792, 1.69, 82 based on C_3F_8 consumed) $(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{CF}_2\cdot\text{CF}(\text{CF}_3)\cdot\text{O}\cdot\text{N}(\text{CF}_3)_2$ (2) (0.197, 0.405, 19.5 based on C_3F_8 consumed) $(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{N}(\text{CF}_3)_2$ (trace) $\text{CF}_2:\text{CF}\cdot\text{CF}_3$ (0.057, 0.380, 16) $(\text{CF}_3)_2\text{NH}$ (trace) $(\text{CF}_3)_2\text{N}\cdot\text{N}(\text{CF}_3)_2$ (small amount)	} ^g
0.828, 2.59	$\text{CF}_2:\text{CHF}$ 0.212, 2.58	108	$(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{CF}_2\cdot\text{CHF}\cdot\text{N}(\text{CF}_3)_2$ (3) (0.687, 1.71, 77 based on C_2HF_3 consumed) $(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{CHF}\cdot\text{CF}_2\cdot\text{N}(\text{CF}_3)_2$ (4) (0.173, 0.430, 19.5 based on C_2HF_3 consumed) $(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{N}(\text{CF}_3)_2$ (0.106, 0.331, 13) $\text{CF}_2:\text{CHF}$ (0.030, 0.360, 14) $(\text{CF}_3)_2\text{NH}$ (trace)	

^a Probably excessive. ^b B.p. 89°C at 762 mmHg (Siwoloboff). ^c This compound was separated by trap-to-trap fractional condensation from two other products with longer g.l.c. retention times which were possibly the telomers $(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot[\text{CF}_2\cdot\text{CF}_2]_x\cdot\text{N}(\text{CF}_3)_2$ ($x = 2$ or 3); an involatile white solid (0.006 g) recovered from the reaction tube possessed an i.r. spectrum virtually identical with that of polytetrafluoroethylene. ^d By mass spectrometry. ^e A small amount of material presumed to be telomeric in nature was also detected by g.l.c. ^f The reaction was slow at room temperature (*ca.* 5% conversion of reactants into products occurred during 6 days), so the mixture was heated at 85°C for 13 h. ^g Isolated as a mixture of adducts which was shown by elemental analysis and ¹⁹F n.m.r. spectroscopy to be a 80.5 : 19.5 molar mixture of (1) and (2) [Found: C, 17.7; N, 6.0. Calc. for a 80.5 : 19.5 molar mixture of (1) and (2): C, 17.75; N, 5.95%]. ^h Isolated as an 80 : 20 mixture (by n.m.r. analysis) of (3) and (4) with b.p. 96°C at 756 mmHg (Siwoloboff).

mmol), trifluoronitromethane (0.40 mmol), trifluoronitrosomethane (0.37 mmol), traces of carbonyl fluoride and silicon tetrafluoride, and bistrifluoromethyl nitroxide (6.16 mmol, 30% recovery).

Reactions of Perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane).—(a) *Pyrolysis.* The diazapentane (0.206 g, 0.644 mmol) was passed at 1 mmHg pressure through a 100×0.9 cm platinum tube heated to 180°C over 60 cm of its length. The purple product was fractionated *in vacuo* to remove bistrifluoromethyl nitroxide and the colourless higher-boiling material was recycled through the platinum tube. This procedure was repeated until no more bistrifluoromethyl nitroxide was produced. The combined products were subjected to trap-to-trap fractional condensation, *in vacuo*, to give (i) (-96°C trap) tetrakis-

anhydrous hydrogen iodide (0.399 g, 3.12 mmol). The tube was sealed, allowed to warm to room temperature, and stored for 1 day. The volatile product was fractionated to give *NN*-bistrifluoromethylhydroxylamine (0.118 g, 0.699 mmol 100%), bistrifluoromethylamine (0.102 g, 0.666 mmol, 95%), hydrogen iodide (0.162 g, 1.27 mmol), and traces of silicon tetrafluoride. Iodine (0.153 g, 0.603 mmol, 86% based on the diazapentane) was recovered from the reaction vessel and estimated volumetrically (thiosulphate titration).

Immediate liberation of iodine occurred when perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (0.177 g, 0.553 mmol) was added to a solution of potassium iodide (0.22 g, 1.33 mmol) in 9 : 1 v/v acetone-water (5 ml) at room temperature. After the solution had been stored for 1 h,

the iodine (0.112 g, 0.441 mmol, 80%) formed was estimated by titration against 0.1002M-sodium thiosulphate.

(c) *With nitric oxide.* A mixture of nitric oxide (0.052 g, 1.73 mmol) and perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (0.268 g, 0.839 mmole) was kept in a Pyrex ampoule (50 ml) at room temperature in the dark for

mmol \equiv 92% yield of *O*-nitrosobistrifluoromethylhydroxylamine).

(d) *With polyfluoro-olefins.* Equimolar amounts of perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) and a polyfluoro-olefin were condensed, separately and *in vacuo*, into a cold (-196°C) Pyrex tube (50 ml), which was then

TABLE 2

N.m.r. data for previously unreported compounds containing $(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot$ and $(\text{CF}_3)_2\text{N}\cdot$ groups					
Compound	Nuclei	P.p.m. ^a	Rel. int.	Multiplicity	
$(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{N}(\text{CF}_3)_2$ ^b	1	-8.3	3	unresolved t (br)	
	2	+15.1	1	s (br)	
	3	+18.0	1	septet ($J_{3,4}$ 15.2 Hz) (br)	
	4	-23.5	3	unresolved t of t (br)	
$(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{CFCl}\cdot\text{CF}_2\cdot\text{N}(\text{CF}_3)_2$	1	-10.0	6	complex (br)	
	2	-3.5	1	s (br)	
	3	+13.0	2	complex AB pattern	
	4	-24.0	6	t of d ($J_{3,4}$ 16.5, $J_{2,4}$ 10.7 Hz)	
$(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{CF}(\text{CF}_3)\cdot\text{CF}_2\cdot\text{N}(\text{CF}_3)_2$	1	-9.3	6	complex (br)	
	2	+55.2	1	unresolved (br)	
	3	-1.0	3	complex (br)	
	4	+11.3	2	Ab pattern (J 250 Hz)	
	5	-24.0	6	t of d ($J_{4,5}$ 15.0, $J_{2,5}$ 9.9 Hz)	
$(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{CF}_2\cdot\text{CHF}\cdot\text{N}(\text{CF}_3)_2$	1	-8.3	6	t ($J_{1,2}$ 8.2 Hz)	
	2	+9.7	2	unresolved d of septets	
	3	+91.0	1	d of septets or nonets	
	4	-20.1	6	q ($J_{2,4} = J_{3,4} = 7.5$ Hz)	
	5	+1.16	6	d of t ($J_{3,5}$ 43.2, $J_{2,5}$ 6.0 Hz)	
$(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{CHF}\cdot\text{CF}_2\cdot\text{N}(\text{CF}_3)_2$	1	-8.0	6	s (br)	
	2	+67.7	1	d (br)	
	3	+20.0	2	complex (br)	
	4	-22.5	6	t of d ($J_{3,4}$ 12.7, $J_{2,4}$ 3.4 Hz)	
	5	+1.03	6	d of t ($J_{2,5}$ 57.0, $J_{3,5}$ 6.0 Hz)	

^a ¹⁹F Ref. external $\text{CF}_3\cdot\text{CO}_2\text{H}$; ¹H ref. external C_6H_6 . ^b Note that the chemical shift data reported previously⁶ for the bistrifluoromethyl nitroxide-tetrafluoroethylene adduct $(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{O}\cdot\text{N}(\text{CF}_3)_2$ are incorrect, the values for δ_1 and δ_2 being -8.6 and $+15.5$ p.p.m., respectively, not $+0.86$ and $+1.55$.

4 days. Fractionation of the pale brown, volatile product gave nitric oxide (0.005 g, 0.167 mmol) and a mixture (1.76 mmol) shown by i.r. spectroscopy to contain *O*-nitroso-*NN*-bistrifluoromethylhydroxylamine, bistrifluoromethylnitrosamine, and traces of bistrifluoromethylamine. The mixture of $(\text{CF}_3)_2\text{N}$ -compounds was shaken with mercury and an excess of hydrochloric acid (50% v/v) for 24 h, then the volatile product was fractionated to give *NN*-bistrifluoromethylhydroxylamine (0.130 g, 0.770

sealed and stored in the dark at room temperature or, in the case of perfluoropropene, at 85°C . The product was subjected to trap-to-trap fractional condensation *in vacuo* and the fractions were analysed by standard techniques. The results are summarised in Table 1. N.m.r. data for the new compounds obtained are listed in Table 2.

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