Nitroxide Chemistry. Part VII.[1] Synthesis and Some Reactions of Perfluoro-2,5-diazahexane 2,5-Dioxyl[2]

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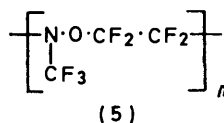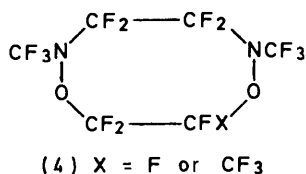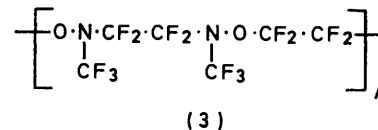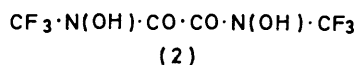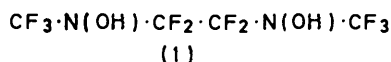
Oxidation by potassium permanganate of aqueous perfluoro-2,5-diazahexane-2,5-diol obtained by hydrolysis of a trifluoronitrosomethane–tetrafluoroethylene–phosphorus trichloride 2 : 1 : 1 adduct yields perfluoro-2,5-diazahexane 2,5-dioxyl. The dioxyl reacts with hydrogen bromide to give the parent diol, with nitric oxide to yield perfluoro-2,5-dinitrito-2,5-diazahexane, with tetrafluoroethylene to provide perfluoro-(2,5-dimethyl-1,6-dioxa-2,5-diazacyclo-octane) and an alternating copolymer, $-[O \cdot N(CF_3) \cdot CF_2CF_2 \cdot N(CF_3) \cdot O \cdot CF_2CF_2]-_n$, with perfluoro-propene to afford perfluoro-(2,5,7-trimethyl-1,6-dioxa-2,5-diazacyclo-octane) and a copolymer, and with trifluoronitrosomethane or perfluoro-1-nitrosopropane to yield perfluoro-(2,5-dimethyl-1-oxa-2,5-diazacyclo-pentane). The last product rapidly oxidises iodide ion to iodine and decomposes slowly at room temperature into perfluoro-(N-methylenemethylamine) and perfluoropoly-[(N-methylenemethylamine) N-oxide]; decomposition in the presence of hydrogen fluoride gives bistrifluoromethylamine and NN-bistrifluoromethylhydroxylamine. Flow pyrolysis of the diazacyclopentane at 155 °C and ca. 1 mmHg pressure yields a complex mixture believed to contain perfluoro-(N-methylenemethylamine) N-oxide.

A laboratory apparatus for the continuous production of trifluoronitrosomethane via pyrolysis of trifluoroacetyl nitrite is described.

THE quest [3,4] for a vulcanising agent that would convert an unsaturated polymer based on the $CF_3 \cdot N\!:\!O/CF_2\!:\!CF_2/CF_2\!:\!CF \cdot CF\!:\!CF_2$ termonomer system into a 'perfect' nitroso-rubber network led to an appraisal of the proposal [5] that alkaline hydrolysis of a $CF_3 \cdot N\!:\!O/CF_2\!:\!CF_2/PCl_3$ 2 : 1 : 1 adduct proceeds via per-fluoro-2,5-diazahexane-2,5-diol (1), since this bis-hydroxylamine is an obvious precursor of the structurally ideal bisnitroxide $\cdot O \cdot N(CF_3) \cdot CF_2 \cdot CF_2 \cdot N(CF_3) \cdot O \cdot$ [4] {cf.[6] $(CF_3)_2N \cdot OH + [O] \longrightarrow (CF_3)_2N \cdot O \cdot$}. In fact, careful

sulphuric acid at 90 °C gives the expected bisnitroxide in high yield.

Perfluoro-2,5-diazahexane 2,5-dioxyl, a deep purple liquid (b.p. 55 °C at 769 mmHg), is the first perfluorin-ated bisnitroxide to be isolated. It can be stored unchanged for at least 3 days as a vapour in the dark at 21 °C in Pyrex, and resembles its purple monofunctional analogue bistrifluoromethyl nitroxide [6,9] in many ways: it seems inert towards air or water at ambient tem-perature, attacks mercury (giving a grey solid that is

CF3·N(OH)·CF2·CF2·N(OH)·CF3

(1)

CF3·N(OH)·CO·CO·N(OH)·CF3

(2)

$-\left[O \cdot N \cdot CF_2 \cdot CF_2 \cdot N \cdot O \cdot CF_2 \cdot CF_2 \right]_n$
        | |
        CF3   CF3

(3)

(4) X = F or CF3

$-\left[N \cdot O \cdot CF_2 \cdot CF_2 \right]_n$
    |
    CF3

(5)

treatment of the 2 : 1 : 1 adduct with water at 0 °C does yield a solution from which the bishydroxylamine (1) (with difficulty) and also a compound believed to possess the structure (2) [7,8] can be isolated, and direct oxidation of the solution with potassium permanganate in dilute

under investigation [10]), combines readily with nitric oxide [forming $CF_3 \cdot N(O \cdot NO) \cdot CF_2 \cdot CF_2 \cdot N(O \cdot NO) \cdot CF_3$], ab-stracts hydrogen atoms from many organic substrates to give its parent hydroxylamine [11] (a conversion best achieved with hydrogen bromide at 0 °C), and reacts

[1] Part VI, R. E. Banks, D. J. Edge, J. Freear, and R. N. Haszeldine, J.C.S. Perkin I, 1974, 721.

[2] Preliminary communication, R. E. Banks, K. C. Eapen, R. N. Haszeldine, P. Mitra, T. Myerscough, and S. Smith, J.C.S. Chem. Comm., 1972, 833.

[3] R. E. Banks, P. A. Carson, and R. N. Haszeldine, J.C.S. Perkin I, 1973, 1111.

[4] R. E. Banks, R. N. Haszeldine, P. Mitra, T. Myerscough, and S. Smith, J. Macromol. Sci., in the press.

[5] A. Ya Yakubovich, P. O. Gitel', Z. N. Lagutina, and F. N. Chelobov, Zhur. obshchei Khim., 1966, 36, 163, proposed the structure $CF_3 \cdot N \cdot O \cdot PCl_3 \cdot O \cdot N(CF_3) \cdot CF_2 \cdot CF_2$ for the adduct. The alternative structure $CF_3 \cdot \overset{+}{N}(\bar{O}) \cdot PCl_3 \cdot \overset{+}{N}(\bar{O})(CF_3) \cdot CF_2 \cdot CF_2$ is favoured by others (ref. 7). Further work is in progress (A. Arfaei, R. E. Banks, R. N. Haszeldine, A. V. Holt, and S. Smith).

[6] S. P. Makarov, A. Ya Yakubovich, S. S. Dubov, and A. N. Medvedev, Doklady Akad. Nauk S.S.S.R., 1965, 160, 1319; W. D. Blackley and R. R. Reinhard, J. Amer. Chem. Soc., 1965, 87, 802; R. E. Banks, R. N. Haszeldine, and M. J. Stevenson, J. Chem. Soc. (C), 1966, 901.

[7] V. A. Ginsburg, L. L. Martynova, M. F. Lebedeva, S. S. Dubov, A. N. Medvedev, and B. I. Tetel'baum, J. Gen. Chem. U.S.S.R., 1967, 37, 1016.

[8] T. Myerscough, Ph.D. Thesis, University of Manchester, 1970.

[9] For reviews of the chemistry of $(CF_3)_2N \cdot O \cdot$, see R. E. Banks and M. G. Barlow, 'Fluorocarbon and Related Chemistry,' Chemical Society Specialist Periodical Reports, vol. 1, 1971, p. 109; vol. 2, 1974, p. 223.

[10] A. Arfaei, work in progress.

[11] The chemistry of $CF_3 \cdot N(OH) \cdot CF_2 \cdot CF_2 \cdot N(OH) \cdot CF_3$ and its alkali-metal derivatives is being explored (R. E. Banks, R. N. Haszeldine, and R. A. Hughes, work in progress).

readily with the perfluoro-olefins CF_2:CFX (X = F or CF_3) and trifluoronitrosomethane.

The reactions involving tetrafluoroethylene and hexafluoropropene lead to the formation of 1 : 1 copolymers [e.g. (3)] and eight-membered heterocycles (4), production of the former being favoured by the use of low temperatures and condensed phase systems; for example, the yield of the diazacyclo-octane (4; X = CF_3) rose from 7%, in a reaction carried out by allowing an equimolar mixture of the bisnitroxide and hexafluoropropene to warm from −196 °C to room temperature, to 63% in one where the bisnitroxide was mixed with an excess of the olefin in the vapour phase at 21 °C and ca. 25 mmHg pressure. Interestingly, the heterocycle (4; X = F) obtained from tetrafluoroethylene was isolated nearly a decade ago from low-molecular-weight material formed in the copolymerization of trifluoronitrosomethane with tetrafluoroethylene;[12] when pyrolysed in a platinum bomb at 480 °C for 15 h, it decomposes quantitatively into an equimolar mixture of carbonyl fluoride and perfluoro-(N-methylenemethylamine), in keeping with the structure assigned.[13-15] The copolymer (3) differs structurally from the corresponding nitroso-rubber (5) prepared from trifluoronitrosomethane and tetrafluoroethylene[14] in that the hetero-atoms are transposed in alternate N−O linkages; this has no marked effect on thermal stability, as expected, since smooth 'unzipping' to carbonyl fluoride and perfluoro-(N-methylenemethylamine) via initial N−O homolysis is feasible. Full details of the copolymerization of perfluoro-2,5-diazahexane 2,5-dioxyl with a variety of olefins and dienes will be reported later.

Reaction with Trifluoronitrosomethane.—Previously,[4] reaction of perfluoro-2,5-diazahexane 2,5-dioxyl with 2 mol. equiv. of trifluoronitrosomethane at 20 °C in the dark for 3 days was found to yield a polymer believed to contain units of the type −N(CF_3)·CF_2·CF_2·N(CF_3)·O− and −N(CF_3)·CF_2·O−, together with volatile material that was examined only cursorily and found to comprise trifluoronitrosomethane, trifluoronitromethane, and perfluoro-(N-methylenemethylamine). Careful examination of the volatile product obtained from a similar reaction (dioxyl : trifluoronitrosomethane ratio 1 : 4, room temperature, 8 days) revealed that it contained the novel cyclic N−O−N compound perfluoro-(2,5-dimethyl-1-oxa-2,5-diazacyclopentane) (6) (isolated in 4% yield), in addition to the compounds detected previously, and traces of trifluoromethyl isocyanate and silicon tetrafluoride [from adventitious hydrolysis of perfluoro-(N-methylenemethylamine)[16]]. By using a

lower reaction temperature (0 °C, 10 days) or a shorter reaction period (20 °C, 1 day), the thermally unstable (see below) N−O−N compound (6) was obtained in much higher yield (46 and 38% yield, respectively). Use of heptafluoro-1-nitrosopropane (0 °C, 14 days) gave only the symmetrical N−O−N compound (6), the n-C_3F_7 group of the nitroso-compound appearing as heptafluoro-1-nitropropane (101% based on 73% consumption of heptafluoro-1-nitrosopropane, and 96% based on quantitative loss of the dioxyl). A similar correspondence between the yields of trifluoronitromethane and the amounts of starting materials consumed was noted in the reactions involving trifluoronitrosomethane. These facts can be accommodated by the reaction pathway shown in the Scheme, which initially follows the mechanism proposed to account for the formation of an equimolar mixture of the acyclic N−O−N compound $(CF_3)_2N$·O·$N(CF_3)_2$ and trifluoronitromethane from bistrifluoromethyl nitroxide and trifluoronitrosomethane.[15]

Perfluoro-(2,5-dimethyl-1-oxa-2,5-diazacyclopentane) (6) is a colourless volatile liquid (extrapolated b.p. 60 °C) that decomposes slowly at room temperature in the absence of light to give 1 mol. equiv. of perfluoro-(N-methylenemethylamine) and a quantitative yield of a gum possessing an elemental analysis and [19]F n.m.r. spectral characteristics consistent with perfluoropoly-[(N-methylenemethylamine)   N-oxide], −[N(CF_3)·O·CF_2]−$_n$; presumably homolytic ring fission at an N−O bond is followed by β-scission of the resultant diradical (7) [see the Scheme; cf.[17] $(CF_3)_2N$·O·$N(CF_3)_2$ $\xrightarrow{\Delta}$ $(CF_3)_2N$·O· + $(CF_3)_2N$· ⟶ $(CF_3)_2N$·$N(CF_3)_2$].

Flow pyrolysis of the diazacyclopentane (6) at 150—200 °C and ca. 1 mmHg pressure in platinum yields trifluoronitrosomethane, carbonyl fluoride, perfluoro-(N-methylenemethylamine), and traces of a yellow gas that possesses i.r. spectral characteristics identical with those reported[18] for a compound thought to be perfluoro-(N-methylenemethylamine) N-oxide; treatment of a mixture of perfluoro-(N-methylenemethylamine) and the yellow material with hydrogen fluoride gives a mixture of NN-bistrifluoromethylamine and NN-bistrifluoromethylhydroxyamine, in keeping[18] with the nitrone assignment. Like its acyclic analogue $(CF_3)_2N$·O·N-$(CF_3)_2$,[17] perfluoro-(2,5-dimethyl-1-oxa-2,5-diazacyclopentane) oxidises iodide ion to iodine rapidly and essentially quantitatively at room temperature. Storage of a mixture of the diazacyclopentane and hydrogen fluoride at room temperature results in the formation of an essentially equimolar mixture of the bistrifluoromethylamino-compounds $(CF_3)_2NH$ and $(CF_3)_2N$·OH, in keeping with the mode of thermal decomposition suggested in the Scheme.

[12] R. E. Banks, R. N. Haszeldine, and M. J. Stevenson, unpublished results; M. J. Stevenson, Ph.D. Thesis, University of Manchester, 1967.
[13] The relative thermo-fragility of the N−O linkage in both monomeric and polymeric fluorocarbon compounds of this type is well known to be of great value in structure determination [see, for example, D. A. Barr, R. N. Haszeldine, and C. J. Willis, *J. Chem. Soc.*, 1961, 1351; R. E. Banks, R. N. Haszeldine, H. Sutcliffe, and C. J. Willis, *ibid.*, 1965, 2506; R. E. Banks, R. N. Haszeldine, and D. R. Taylor, *ibid.*, p. 5602; R. E. Banks, M. G. Barlow, and R. N. Haszeldine, *ibid.*, p. 6149; R. E. Banks, M. G. Barlow, R. N. Haszeldine, and M. K. McCreath, *ibid.*, p. 7203.

[14] D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1955, 1881.
[15] R. E. Banks, R. N. Haszeldine, and M. J. Stevenson, *J. Chem. Soc. (C)*, 1966, 901.
[16] D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1956, 3428.
[17] R. E. Banks, R. N. Haszeldine, and T. Myerscough, *J.C.S. Perkin I*, 1972, 1449.
[18] V. A. Ginsburg, K. N. Smirnov, and M. N. Vasil'eva, *J. Gen. Chem. U.S.S.R.*, 1969, **39**, 1304.

Preparation of Trifluoronitrosomethane.—It has been suggested recently that the preparation of trifluoronitrosomethane *via* pyrolysis of trifluoroacetyl nitrite is too dangerous and inefficient to operate in the laboratory.[19] In our experience this is certainly not the case, and the method we have used for nearly a decade now without mishap is described in the Experimental section; the apparatus and technology are modelled on that used industrially to prepare trifluoronitrosomethane.[20]

HA-100 (^{19}F at 94·1 MHz) instrument, and an A.E.I. MS902 spectrometer, respectively. ^{19}F Chemical shifts (δ_F) are quoted with reference to external trifluoroacetic acid, values to high field being designated positive.

Preparation of Trifluoronitrosomethane (*with* J. V. LATHAM *and* J. MAIRS).—Trifluoroacetyl nitrite[21] (475 g) was prepared by rapidly adding trifluoroacetic anhydride (351 g, 1·67 mol) to stirred, cold (−30 °C) dinitrogen trioxide (124 g, 1·63 mol); the jade-green mixture obtained was stirred at *ca.* −5 °C until its colour changed to pale brown (*ca.* 3 h), formation of the acyl nitrite then being

SCHEME
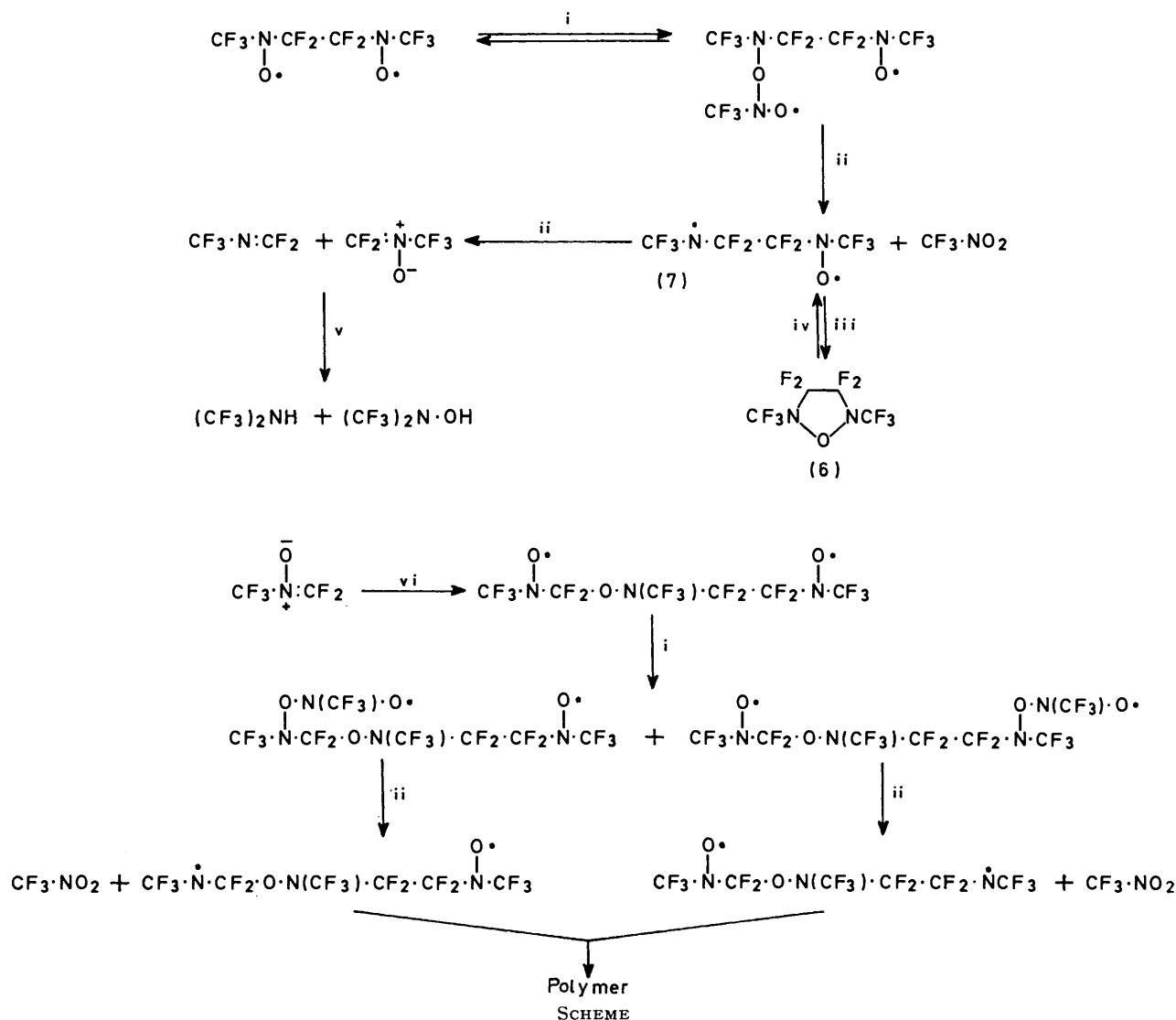
Reagents: i, CF₃·NO; ii, fragmentation; iii, ring closure; iv, N—O homolysis; v, HF; vi, $CF_3 \cdot N(\dot{O}) \cdot CF_2 \cdot CF_2 \cdot N(\dot{O}) \cdot CF_3$

EXPERIMENTAL

I.r., n.m.r., and mass spectra were obtained using a Perkin-Elmer spectrophotometer model 257, a Perkin-Elmer R10 (^{19}F at 56·46 and ^{31}P at 24·29 MHz) or Varian

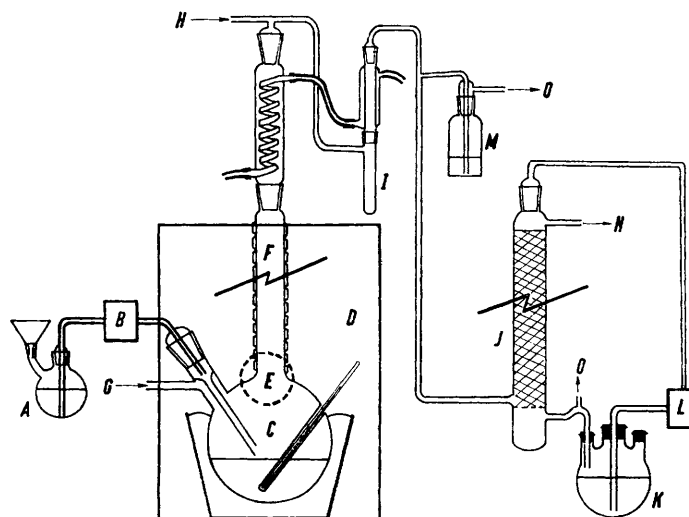[19] P. M. Spaziante, *M.T.P. Int. Rev. Sci.: Inorg. Chem. Ser.* 1, 1972, **3**, 141.

[20] G. H. Crawford and D. E. Rice, U.S.P. 3,162,692/1964; M. C. Henry, C. G. Griffis, and E. C. Stump, *Fluorine Chem. Rev.*, 1967, **1**, 1.

complete. This material was stored in a refrigerator prior to use; isolation of pure trifluoroacetyl nitrite by distillation proved unnecessary since use of the crude material caused no noticeable decrease in the yield of trifluoronitrosomethane. Slow addition of the anhydride to dinitrogen trioxide gives a cloudy, rather than clear, product, and

[21] R. E. Banks, M. G. Barlow, R. N. Haszeldine, and M. K. McCreath, *J. Chem. Soc.* (*C*), 1966, 1350.

leads to inferior yields of trifluoronitrosomethane in the pyrolysis stage.

Trifluoroacetyl nitrite (total 415 g, 2·90 mol) was transferred at a constant rate (80 g h⁻¹) from a Pyrex reservoir A (ca. 100 cm³) (see Figure) to the pyrolysis chamber C by means of a Watson and Marlow H.R. Flow Inducer (type MHRE 72) peristaltic pump B fitted with small-bore silicone tubing (0·5 mm i.d., 1·6 mm o.d.; the glass delivery tube attached to this was 2 mm bore capillary); the silicone tubing deteriorated fairly rapidly and was replaced after each run, which consisted of batchwise pyrolysis of four separate charges of ca. 100 g of the acyl nitrite. [The amount of starting material in A was restricted to minimise possible explosion damage; other safety measures included (i) siting of the whole apparatus in an efficient walk-in fume-cupboard (CF₃·NO is toxic) provided with stout Cobex windows reinforced with steel mesh, and (ii) encasement of the pyrolysis section in a stout three-sided steel box D provided with a Perspex inspection window E

150 g of trifluoroacetyl nitrite and wash out J with dilute hydrochloric acid then water; at the same time, the sodium hydroxide solution in K was replaced. Obviously use of a dual scrubbing section would allow the pyrolysis to proceed without such a break.] The gaseous effluent N from the scrubbing tower was passed through a train comprising a Pyrex trap cooled to −72 °C, to remove most of the 'dimer' (CF₃)₂N·O·NO present, and then two traps cooled to −144 °C to condense the crude trifluoronitrosomethane. After purification by distillation techniques, the contents of the final traps yielded 115 g (1·16 mol, 40%) of trifluoronitrosomethane. The apparatus was provided with vents to the atmosphere at points O; the Drechsel bottle M contained paraffin oil.

Preparation of Perfluoro-2,5-diazahexane 2,5-Dioxyl.— Trifluoronitrosomethane (6·58 g, 66·5 mmol) and tetrafluoroethylene (3·33 g, 33·3 mmol) were condensed separately into a cold (−196 °C) evacuated Pyrex tube (250 cm³) containing phosphorus trichloride (4·57 g, 33·3 mmol);

(6 cm diam.) and a hole to accommodate the trifluoroacetyl nitrite delivery tube.] The pyrolysis section comprised a Pyrex flask C (3 l) fused to a tube F (90 × 5·0 cm) wrapped in an Electrothermal heating tape controlled by a Variac autotransformer, like the Isomantle used to boil (175—179 °C) the FC 43 [Minnesota Mining and Manufacturing Co. trade name for (C₄F₉)₃N] (ca. 200 cm³) in C; the temperature of the FC 43 vapour in tube F was maintained at 190 °C, and the water-cooled condenser surmounting F was examined regularly to check that no diminution in reflux rate occurred (with concomitant increase in explosion hazard). Slow streams of dry nitrogen were introduced at points G and H through p.v.c. tubing (rubber tubing tends to rot owing to attack by vapour from C) to help sweep pyrolysis products through the water-cooled spiral condenser (some FC 43 collected in trap I and was later returned to C) and thence, via p.v.c. tubing, into the bottom of a Pyrex counter-current scrubbing tower J (90 × 5·0 cm) packed with porcelain saddles (1 cm diam.); 5M-sodium hydroxide solution (1 l) was circulated through the scrubber from a reservoir K using a Glen Creston peristaltic pump (model L315) L. [The CO₂-scrubber J tended to become blocked with sodium carbonate, and during extensive runs it was necessary to discontinue temporarily the process (the nitrogen purges were maintained) after pyrolysis of ca.

the tube was sealed and stored at ca. −35 °C for 5 days in the dark. A duplicate experiment was carried out simultaneously, and the combined volatile products were shown by a combination of trap-to-trap fractional condensation and analytical techniques [i.r. spectroscopy, M determination (Regnault)] to comprise trifluoronitrosomethane, tetrafluoroethylene (total 55·6 mmol), perfluoro-(2-methyl-1,2-oxazetidine) (15·8 mmol), unknown material (0·71 g; $\lambda_{max.}$ 5·52, 5·61, and 7·35—8·47 μm) condensing at −46 °C, and an unidentified liquid (7·9 g; −23 °C trap) that partly changed into a gel on storage in glass [δ_F −18·3 (s) and −14·6br (complex) p.p.m.; δ_P (ext. H₃PO₄) −2·0br (s) p.p.m.]. The combined involatile products were distilled to yield an adduct of composition 2CF₃·NO,C₂F₄,PCl₃ (8·17 g, 18·8 mmol, 28%) (Found: C, 11·3; F, 43·1; N, 6·7. Calc. for C₄Cl₃F₁₀N₂O₂P: C, 11·0; F, 43·5; N, 6·4%), b.p. 62 °C at 15 mmHg (lit.,[5] 64 °C at 20 mmHg), δ_F (neat liq.) −14·0 (t, J 13·6 Hz, with further splitting, CF₃), +35·8br (s, CF₂) (rel. int. 3 : 2), and −12·3br (t, J 14 Hz, impurity) p.p.m., δ_P (ext. H₃PO₄) +22·0br (s) p.p.m. (lit.,[7] δ_F −14·5 and +35·0, δ_P +9·2 p.p.m.), with a highest mass peak corresponding to C₄Cl₂F₉N₂O₂P⁺·. The yield of the 2CF₃·NO–C₂F₄–PCl₃ adduct was increased to 80% by keeping the reactants at −32 °C for 19 days; thus adduct (43·46 g) was obtained from CF₃·NO (24·96 g),

C_2F_4 (12·61 g), and PCl_3 (21·43 g) contained in a 1150 cm³ Pyrex ampoule.

Water (5 cm³) was added dropwise to a sample of the $2CF_3 \cdot NO-C_2F_4-PCl_3$ adduct (0·92 g, 2·11 mmol) cooled to 0 °C. The solution obtained was added dropwise to a hot (90 °C) solution of potassium permanganate (1·0 g) in $2M-H_2SO_4$ (10 cm³) in a flask (50 cm³) fitted with an air-bleed and a water-cooled reflux condenser connected, *via* three cold (−196 °C) traps, to a vacuum system to enable the pressure in the apparatus to be reduced to *ca.* 200 mmHg. The reaction was allowed to proceed for 5 h, during which time the permanganate was replenished by the addition of a saturated aqueous solution (15 cm³); fractionation of the product collected in the cold traps gave a mixture (0·212 g) of chlorine, hydrogen chloride, trifluoro-nitromethane, and carbon dioxide, and *perfluoro-2,5-diaza-hexane 2,5-dioxyl* (0·52 g, 1·75 mmol, 83%) [Found: C, 16·4; N, 9·5%; *M* (Regnault), 296. $C_4F_{10}N_2O_2$ requires C, 16·1; N, 9·4%; *M*, 298], b.p. 55 °C at 769 mmHg (Siwoloboff), $\lambda_{max.}$ (vapour) 7·19w, 7·68s, 8·08s, 8·51m, 9·12w, 10·81w, 11·53w, and 13·53w μm, δ_F (neat liq.) −8·0br (s, CF_3) and +28·0br (s, CF_2) p.p.m. (rel. int. 3 : 2), *m/e* 298 ($M^{+\cdot}$, <1%), 149 ($C_2F_5NO^+$, 5), 133 ($C_2F_5N^+$, 5), 114 ($C_2F_4N^+$, 25), 100 ($C_2F_4^+$, 5), 92 ($C_2F_2NO^+$, 6), and 69 (CF_3^+, 100). The e.s.r. spectrum of the dioxyl will be discussed in detail later.[22]

Scale-up (×7) of the dioxyl preparation resulted in the formation of yellowish orange material which co-condensed with the dioxyl (at −96 °C at <2 mmHg); when the trap containing the mixture was allowed to warm up, a violent explosion occurred. This hazard can be eliminated by adding a saturated aqueous solution of silver nitrate to the $2CF_3 \cdot NO-C_2F_4-PCl_3$ adduct hydrolysate, until no more silver chloride precipitates, prior to the oxidation stage.

Reactions of Perfluoro-2,5-diazahexane 2,5-Dioxyl.—
(a) *With hydrogen bromide.* The dioxyl (0·894 g, 3·00 mmol) was condensed, *in vacuo*, into a cold (−196 °C) Pyrex tube (300 cm³) containing hydrogen bromide (0·486 g, 6·00 mmol), which was sealed and transferred to a bath at 0 °C. A vigorous reaction occurred as the tube warmed up, and bromine was liberated. Fractionation of the product gave *perfluoro-2,5-diazahexane-2,5-diol* (0·750 g, 2·50 mmol, 83%) (Found: C, 16·1; H, 0·8; F, 63·0; N, 9·6. $C_4H_2F_{10}N_2O_2$ requires C, 16·0; H, 0·7; F, 63·3; N, 9·3%), a hygroscopic, crystalline solid, m.p. 43 °C, $\lambda_{max.}$ (vapour at 60 °C) 2·78 μm [O–H str.; *cf.*[23] $(CF_3)_2N \cdot O-H$, 2·76 μm], δ_F (*ca.* 20% w/v soln. in dioxan) −10·8 (t, CF_3) and +27·0 (q, CF_2) p.p.m. (rel. int. 3 : 2).

(b) *With nitric oxide.* Fractionation of the brown liquid obtained by condensing the dioxyl (0·331 g, 1·11 mmol) onto nitric oxide (0·068 g, 2·25 mmol) at −196 °C, *in vacuo* (50 cm³ Pyrex reaction tube), and allowing the mixture to warm to room temperature, gave *perfluoro-2,5-dinitrito-2,5-diazahexane* (0·366 g, 1·02 mmol, 92%) (Found: C, 13·5; N, 15·7. $C_4F_{10}N_4O_4$ requires C, 13·4; N, 15·65%), b.p. 90 °C at 769 mmHg (Siwoloboff), $\lambda_{max.}$ (vapour) 5·48 and 5·55 μm doublet [O-NO group; *cf.*[24] $(CF_3)_2N \cdot O \cdot NO$, 5·47 and 5·55 μm doublet], δ_F (neat liq.) −11·5br (s, CF_3) and +22·9br (s, CF_2) p.p.m. (rel. int. 3 : 2).

(c) *With tetrafluoroethylene.* A mixture of the dioxyl (0·337 g, 1·13 mmol) and tetrafluoroethylene (0·114 g, 1·14 mmol), prepared by condensing each reactant separately into a Pyrex tube (50 cm³) cooled in liquid nitrogen,

[22] R. E. Banks, D. J. Edge, R. N. Haszeldine, T. Myerscough, and A. J. Parker, in preparation.

was allowed to warm from −196 °C to room temperature. After 1 h the purple colour of the dioxyl had almost disappeared; 18 h later, the product was colourless, and the volatile material was removed, leaving a colourless viscous 1 : 1 copolymer, *perfluoropoly(oxy-N-methyliminoethylene-N-methylimino-oxyethylene)* (0·420 g, 93%) [Found: C, 18·3; N, 7·2. $(C_6F_{14}N_2O_2)_n$ requires C, 18·1; N, 7·0%], which was recovered from the reaction vessel by dissolution in 1,1,2-trichlorotrifluoroethane. The copolymer showed negligible i.r. absorption at wavelengths below 7·27 μm, δ_F (*ca.* 50% soln. in $CF_2Cl \cdot CFCl_2$) −12·3br (m, CF_3), +14·0br (s, $\cdot N \cdot O \cdot CF_2 \cdot$), and +21·6br (s, $\cdot CF_2 \cdot N \cdot O \cdot$) p.p.m. (rel. int. 3 : 2 : 2), and when heated at 150 °C in the inlet of a mass spectrometer gave a spectrum showing a series of peaks at *m/e* $n \times 398$ [the highest peak occurred at *m/e* >4000; the base peak corresponded to $C_6F_{13}N_2O^+$ (*m/e* 363)]. Fractionation of the volatile product gave tetrafluoroethylene (0·064 mmol, 6% recovery), traces of trifluoronitroso-methane, trifluoromethyl isocyanate, and perfluoro-(*N*-methylenemethylamine), and perfluoro-(2,5-dimethyl-1,6-dioxa-2,5-diazacyclo-octane) (0·015 g, 0·038 mmol, 3%), which showed no i.r. absorption below 6·9 μm, δ_F −10·9 (m, CF_3), +18·9 ($|J_{AB}|$ *ca.* 150 Hz, $\cdot O \cdot CF_2$), and +33·0 ($|J_{AB}|$ *ca.* 210 Hz, $\cdot N \cdot CF_2 \cdot$), possessing i.r. and ^{19}F n.m.r. spectra identical with those of an analytically pure sample, b.p. 100·5 °C at 758 mmHg, isolated from the involatile product formed in the copolymerization of trifluoronitroso-methane with tetrafluoroethylene.[12]

A sample of the 1 : 1 copolymer (0·0884 g) was placed near the sealed end of a Pyrex tube (20 × 2·5 cm), which was connected to a vacuum system *via* a cold (−196 °C) trap. The tube and trap were evacuated then isolated from the vacuum system, and a furnace at 400 °C placed over the tube. After 2 h, the product (0·0864 g) that collected in the cold trap was examined by i.r. spectroscopy and g.l.c. (4 m Kel-F No. 10 oil–Celite; 21 °C) and shown to be an equimolar mixture of perfluoro-(*N*-methylene-methylamine) and carbonyl fluoride.

(d) *With perfluoropropene.* The dioxyl (0·894 g, 3·00 mmol) was condensed, *in vacuo*, into a cold (−196 °C) Pyrex tube (300 cm³) containing perfluoropropene (0·495 g, 3·30 mmol). The tube was sealed and kept at 20 °C, in the dark, for 6 days. Fractionation of the volatile product gave perfluoropropene (0·28 mmol, 8·5% recovery) and *perfluoro-(2,5,7-trimethyl-1,6-dioxa-2,5-diazacyclo-octane)* (0·090 g, 0·20 mmol, 7%) (Found: C, 19·0; F, 64·9; N, 6·2%; M^+, 448. $C_7F_{16}N_2O_2$ requires C, 18·75; F, 67·8; N, 6·25%; *M*, 448), δ_F −11·8 (m, $CF_3 \cdot N \cdot$), +3·4 (m, $\cdot CF \cdot CF_3$), *ca.* +12·0br (m, $\cdot O \cdot CF_2 \cdot$), *ca.* +32·0br (m, $\cdot N \cdot CF_2 \cdot$), and +67·0 (m, $\cdot O \cdot CF \cdot CF_3$) p.p.m. (rel. int. 6 : 3 : 2 : 4 : 1), which showed only negligible i.r. absorption at wavelengths below 7·3 μm. A transparent gummy 1 : 1 *copolymer* (1·16 g) (Found: C, 18·8; F, 68·3; N, 6·1. $C_7F_{16}N_2O_2$ requires C, 18·75; F, 67·8; N, 6·25%) was recovered from the residue by dissolving it in 1,1,2-tri-chlorotrifluoroethane.

Perfluoropropene (0·6435 g, 4·287 mmol) contained in a cold finger (−196 °C) attached to a Pyrex bulb (5 l) containing perfluoro-2,5-diazahexane 2,5-dioxyl (0·213 g, 0·715 mmol) and shielded from light was vaporised rapidly, and the mixture of reactants formed was left in the dark at

[23] G. G. Flaskerud and J. M. Shreeve, *Inorg. Chem.*, 1969, **8**, 2065.
[24] R. N. Haszeldine and B. J. H. Mattinson, *J. Chem. Soc.*, 1955, 4172; 1957, 1741.

room temperature for 7 days. Fractionation of the volatile product gave the dioxyl (0·441 mmol, 62% recovery), perfluoropropene (4·00 mmol), unknown material (0·019 g), and perfluoro-(2,5,7-trimethyl-1,6-dioxa-2,5-diaza-cyclo-octane) (0·077 g, 0·17 mmol, 63% based on dioxyl consumed).

(e) *With trifluoronitrosomethane.* The dioxyl (1·49 g, 5·00 mmol) and trifluoronitrosomethane (1·98 g, 20·0 mmol) were condensed separately, *in vacuo*, into a cold (−196 °C) Pyrex tube (300 cm^3). The tube was sealed and left in the dark at room temperature for 8 days. Trap-to-trap fractional condensation of the volatile product, *in vacuo*, gave (i) a mixture (−196 °C trap) of trifluoronitroso-methane (1·32 g, 13·3 mmol, 67% recovery), trifluoronitro-methane (0·53 g, 4·61 mmol), perfluoro-(N-methylene-methylamine) (0·35 g, 2·63 mmol), and traces of silicon tetrafluoride; (ii) a mixture (−140 °C trap) comprising trifluoronitromethane (0·14 g, 1·22 mmol), perfluoro-(N-methylenemethylamine) (0·06 g, 0·45 mmol), and a trace of trifluoronitrosomethane and trifluoromethyl isocyanate [fractions (i) and (ii) were analysed by i.r. and g.l.c. techniques]; and (iii) *perfluoro-(2,5-dimethyl-1-oxa-2,5-diaza-cyclopentane)* (−72 °C trap) (0·06 g, 0·21 mmol, 4%) [Found: C, 17·0; F, 67·1; N, 9·9%; *M* (Regnault), 281. $C_4F_{10}N_2O$ requires C, 17·0; F, 67·4; N, 9·9%; *M*, 282], extrapolated b.p. (isoteniscope) 60 °C at 760 mmHg, $\lambda_{max.}$ (vapour) 7·42w, 7·70s, 8·00vs, 8·24m, and 8·40w μm, δ_F (neat liq. at 0 °C) −9·5 (t, *J* 4·2 Hz, CF$_3$) and +25·6 (m, CF$_2$) p.p.m. (rel. int. 3 : 2). A pale purple gum (0·96 g) recovered from the reaction vessel was shown by n.m.r. [δ_F (*ca.* 25% w/v soln. in CF$_2$Cl·CFCl$_2$) −12·7br (s, C*F$_3$*·N·CF$_2$·CF$_2$·), −11·5br (s, C*F$_3$*·N·CF$_2$·O·), −5·0br (s, CF$_3$·N·C*F$_2$*·O·), and +21·5br (s, CF$_3$·N·C*F$_2$*·C*F$_2$*·) p.p.m.] and mass spectrometry [4] to be a polymer built up from the repeating units ·N(CF$_3$)·O·CF$_2$· and ·N(CF$_3$)·O·N(CF$_3$)·CF$_2$·CF$_2$·.

The reaction was repeated, using trifluoronitrosomethane (1·98 g, 20·0 mmol) and the dioxyl (1·49 g, 5·0 mmol) at room temperature in the dark for 1 day (100 cm^3 Pyrex reaction tube, calculated initial pressure *ca.* 5 atm). The product comprised perfluoro-(2,5-dimethyl-1-oxa-2,5-diaza-cyclopentane) (1·88 mmol, 38%), trifluoronitromethane (5·68 mmol), perfluoro-(N-methylenemethylamine) (1·03 mmol), trifluoronitrosomethane (14·35 mmol, 72% recovery), traces of silicon tetrafluoride, trifluoromethyl isocyanate, and perfluoro-2,5-diazahexane 2,5-dioxyl, and a purplish polymer (0·64 g) of the above type.

Using the same molar ratio of reactants [CF$_3$·NO (47·0 mmol), dioxyl (10·7 mmol)] under the same conditions (300 cm^3 Pyrex tube) except a reaction temperature of 0 °C and duration of 10 days, the product comprised perfluoro-(2,5-dimethyl-1-oxa-2,5-diazacyclopentane) (4·91 mmol, 46%), trifluoronitromethane (10·8 mmol), perfluoro-(N-methylenemethylamine) (2·15 mmol), trifluoronitroso-methane (34·9 mmol, 74% recovery), polymer (0·51 g), and an unidentified liquid (0·30 g).

(f) *With heptafluoro-1-nitrosopropane.* A mixture of the dioxyl (0·33 g, 1·11 mmol) and the nitroso-compound (0·29 g, 1·46 mmol), sealed in a Pyrex tube (20 cm^3), was kept in the dark at 0 °C for 2 weeks. By a combination of fractionation and i.r. and g.l.c. analysis, the volatile product was shown to contain perfluoro-(2,5-dimethyl-1-oxa-2,5-diazacyclopentane) (0·35 mmol, 31%), perfluoro-(N-methylenemethylamine) (0·30 mmol), heptafluoro-1-nitro-propane (1·07 mmol, 101% based on n-C$_3$F$_7$·NO consumed),

and heptafluoro-1-nitrosopropane (0·40 mmol, 27%). A pale purple, viscous liquid (*ca.* 0·15 g) remained in the reaction vessel.

Reactions of Perfluoro-(2,5-dimethyl-1-oxa-2,5-diazacyclo-pentane).—(a) *With iodide ion.* The heterocycle (0·108 g, 0·383 mmol) was shaken with a solution of potassium iodide (0·40 g, 2·4 mmol) in acetone (5 cm^3) containing 10% of water for 1·5 h at room temperature. The amount of iodine liberated [0·091 g, 0·358 mmol, 93·5% based on
1 $\overline{CF_3 \cdot N \cdot CF_2 \cdot CF_2 \cdot N(CF_3) \cdot O} \equiv 1$ I$_2$] was estimated by standard volumetric techniques using aqueous 0·100M-Na$_2$S$_2$O$_3$.

(b) *With hydrogen fluoride.* An excess of hydrogen fluoride [produced by heating anhydrous KHF$_2$ (0·62 g, 8·0 mmol) at *ca.* 600 °C in a copper tube] was condensed, *in vacuo*, into a cold (−196 °C) stainless steel autoclave (16 cm^3) containing the heterocycle (0·357 g, 1·27 mmol). The autoclave was sealed and kept at room temperature for 15 h. Volatile product was transferred to a vacuum system *via* a 6·0 × 1·0 cm tube packed with anhydrous potassium fluoride, and was fractionated to give bistri-fluoromethylamine (0·05 g, 0·33 mmol, 87% based on the heterocycle consumed) (identified by i.r. spectroscopy) and a mixture that was shown by i.r. and molecular weight determination (Regnault) to contain perfluoro-(2,5-di-methyl-1-oxa-2,5-diazacyclopentane) (0·25 g, 0·89 mmol, 70% recovery) and NN-bistrifluoromethylhydroxylamine (0·06 g, 0·36 mmol, 95%).

(c) *Pyrolysis.* (i) Static. A sample of the heterocycle (0·561 g, 1·99 mmol) was kept in a Pyrex ampoule (25 cm^3) for 5 weeks at room temperature in a dark cupboard. Fractionation of the volatile product gave starting material (0·016 g, 0·057 mmol, 3% recovery) and perfluoro-(N-methylenemethylamine) (0·254 g, 1·91 mmol, 99%). *Perfluoropoly-[(N-methylenemethylamine) N-oxide]* (0·283 g, 97%) [Found: C, 16·1; F, 63·7; N, 9·4. (C$_2$F$_5$NO)$_n$ requires C, 16·1; F, 63·8; N, 9·4%], a colourless gum, δ_F (*ca.* 35% w/v soln. in CF$_2$Cl·CFCl$_2$) −11·2br (s, CF$_3$) and −4·5br (s, CF$_2$) p.p.m. (rel. int. 3 : 2), remained in the reaction tube.

The pyrolysis was repeated at 65 °C for 3 days, using perfluoro-(2,5-dimethyl-1-oxa-2,5-diazacyclopentane) (0·302 g, 1·07 mmol), to give perfluoro-(N-methylenemethylamine) (0·95 mmol, 96%), starting material (0·08 mmol, 7·5% recovery), and perfluoropoly-[(N-methylenemethylamine) N-oxide] (0·135 g, 92%).

(ii) Dynamic. Perfluoro-(2,5-dimethyl-1-oxa-2,5-diaza-cyclopentane) (1·00 g, 3·55 mmol) vapour was passed at *ca.* 1 mmHg pressure through a platinum tube (100 × 0·7 cm) heated to 155 °C over 56 cm of its length and connected to a vacuum system *via* two cold (−196 °C) traps. The condensate from the traps was subjected to fractional condensation, *in vacuo*, to give (i) a mixture (0·18 mmol) (−196 °C trap) shown by i.r. spectroscopy to contain about equal proportions of trifluoronitrosomethane, perfluoro-(N-methylenemethylamine), and carbonyl fluoride, (ii) per-fluoro-(N-methylenemethylamine) (0·026 g, 0·195 mmol) (−140 °C trap) contaminated with trifluoromethyl iso-cyanate, (iii) a pale yellow gas (1·20 mmol) (−120 °C trap) that was found by i.r. spectroscopy to contain perfluoro-(N-methylenemethylamine) (colourless) and the compound believed to be perfluoro-(N-methylenemethylamine) N-oxide,[18] and (iv) perfluoro-(2,5-dimethyl-1-oxa-2,5-diaza-cyclopentane) (0·70 g, 2·49 mmol, 70% recovery).

A yellow mixture of perfluoro-(N-methylenemethyl-amine) and the nitrone from a similar pyrolysis conducted at 200 °C (2·74 mmol; collected in a —120 °C trap) was sealed in a stainless steel autoclave (16 cm³) with anhydrous hydrogen fluoride (8·0 mmol) (from KHF₂ at 600 °C), and the autoclave kept at room temperature for 1 h. The volatile product was transferred to a vacuum system *via* a tube (6·0 × 1·0 cm) packed with anhydrous potassium fluoride and was shown by i.r. spectroscopy and g.l.c. analysis to contain NN-bistrifluoromethylhydroxylamine (0·8 mmol) and bistrifluoromethylamine (1·90 mmol).