Reactions of Perfluoronitroxides with Sulphur Dioxide [1]

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Perfluoro-2,5-diazahexane 2,5-dioxyl reacts with sulphur dioxide and with sulphur tetrafluoride to give the 1:1 cyclic adducts perfluoro(4,7-dimethyl-1,3-dioxa-2-thia-4,7-diazacycloheptane 2,2-dioxide) and perfluoro(4,7-dimethyl-1,3-dioxa-2-tetrafluorothia-4,7-diazacycloheptane), respectively. Perfluoro(4,7-dimethyl-1,3-dioxa-2-thia-4,7-diazacycloheptane 2,2-dioxide) which oxidises iodide ion to iodine at room temperature, is stable to hydrolysis by aqueous potassium hydroxide at 120 °C. It is stable to u.v. irradiation, but flow pyrolysis at 350 °C and ca. 1 mmHg pressure gives trifluoronitrosomethane, perfluoro(2-methyl-1,2-oxazetidine), carbonyl fluoride, perfluoro(N-methylenemethylamine), and sulphur dioxide. It reacts with triphenylphosphine to give perfluoro(3,6-dimethyl-1-oxa-2-thia-3,6-diazacyclohexane 2,2-dioxide), perfluoro(2,5-dimethyl-1-thia-2,5-diazacyclopentane 1,1-dioxide) and triphenylphosphine oxide. Bis(trifluoromethyl) nitroxide reacts with sulphur dioxide to give the 2:1 adduct perfluoro(2,6-dimethyl-3,5-dioxa-4-thia-2,6-diazaheptane 4,4-dioxide), flow pyrolysis of which at 350 °C and ca. 1 mmHg gives only bis(trifluoromethyl) nitroxide and sulphur dioxide. Perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) reacts with sulphur dioxide giving perfluoro(2,5-dimethyl-3-oxa-4-thia-2,5-diazahexane 4,4-dioxide).

The radicals perfluoro-2,5-diazahexane 2,5-dioxyl, $ON(CF_3)CF_2CF_2N(CF_3)O$, and its monofunctional analogue bis(trifluoromethyl) nitroxide, $(CF_3)_2NO$, react readily with fluoro-olefins [2,3] yielding mixtures of 1:1 alternating co-polymers and 1:1 cyclic adducts, and 2:1 nitroxide–olefin adducts, respectively. In some cases, reaction of bis(trifluoromethyl) nitroxide with a compound of an element of variable valency leads to an increase in the oxidation state of that element,[4] e.g. reactions with sulphur dioxide [5] and with sulphur tetrafluoride [6] give 2:1 adducts. The reactions of the dioxyl with sulphur dioxide and with sulphur tetrafluoride have now been investigated as possible routes to new copolymers and heterocyclic compounds.

Results and Discussion

The exothermic, liquid-phase reaction of sulphur dioxide with the dioxyl proceeds rapidly as a mixture of the reactants is allowed to warm from -196 °C to room temperature, giving, virtually quantitatively, the 1:1 cyclic adduct perfluoro(4,7-dimethyl-1,3-dioxa-2-thia-4,7-diazacycloheptane 2,2-dioxide) (1). Under similar conditions, reaction of the dioxyl with sulphur tetrafluoride gives perfluoro(4,7-dimethyl-1,3-dioxa-2-tetrafluorothia-4,7-diazacycloheptane) (2) in good yield. In neither case was a copolymer formed. In this respect these reactions differ from those of the dioxyl with tetrafluoroethene and hexafluoropropene in which the formation of copolymers is favoured at low temperatures in condensed systems and only small amounts (less than 10%) of the cyclic adducts are formed.[2]

The reaction of the dioxyl with sulphur dioxide proceeded much more easily than expected from the reported [5] investigation of the analogous reaction between bis(trifluoromethyl) nitroxide and sulphur dioxide in which the reaction temperature used was 180 °C and the yield of the 2:1 adduct, perfluoro(2,6-dimethyl-3,5-dioxa-4-thia-2,6-diazaheptane 4,4-dioxide) (3), was only 44% after 10 h. Reinvestigation of the latter reaction shows that it proceeds slowly in the liquid phase at room temperature giving virtually quantitative yields of compound (3) after 3 days. The stability of the adduct to hydrolysis has been noted.[7] Flow pyrolysis of compound (3) at 350 °C and ca. 1 mmHg in platinum gives only bis(trifluoromethyl) nitroxide and sulphur dioxide. Condensation of the purple pyrolysis products into a tube containing an excess of
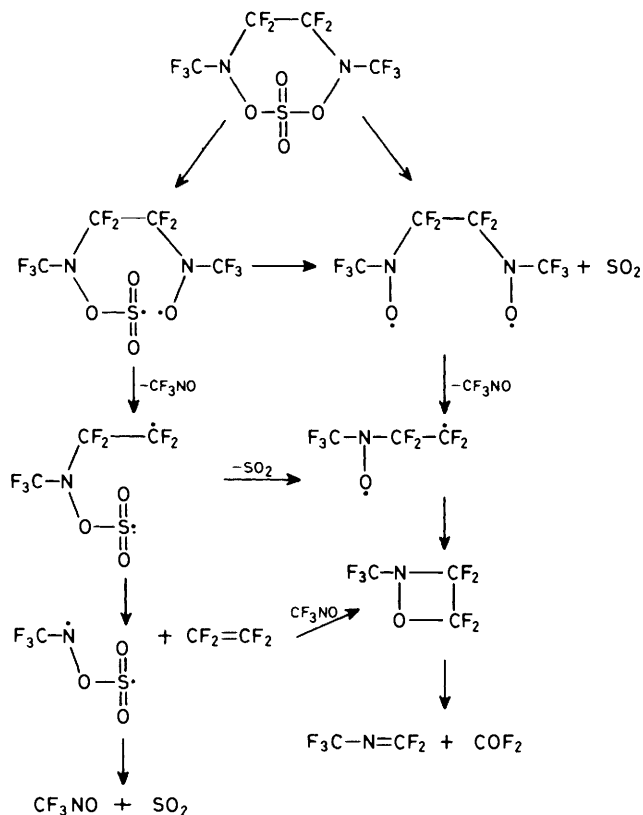

(1)

(CF$_3$)$_2$NOSO$_2$ON(CF$_3$)$_2$

(3)

(2)

(CF$_3$)$_2$NOSO$_2$N(CF$_3$)$_2$

(4)

(5)

(6)
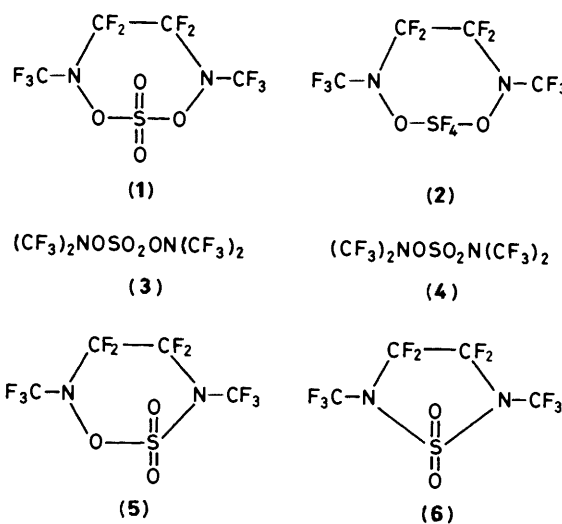
tetrachloroethene, which reacts rapidly with the nitroxide to give a 2:1 nitroxide–olefin adduct, gave, on warming to room temperature, only the adduct and sulphur dioxide.

Sulphur dioxide reacts cleanly with perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) at 70 °C to give perfluoro(2,5-dimethyl-3-oxa-4-thia-2,5-diazahexane 4,4-dioxide) (4). This reaction is analogous to those between the diazapentane and fluoro-olefins.[8]

Formulation of the adducts (1) and (2) as seven- rather than five-membered [e.g. $CF_3\overset{+}{N}(\overset{-}{O})CF_2CF_2\overset{+}{N}(\overset{-}{O})(CF_3)SO_2$] heterocycles is based on spectroscopic evidence. The i.r. spectrum of (1) shows only one strong absorption (6.73 μm, $-SO_2-$ asymm. str.), and that of (2) shows none, at wavelengths below 7 μm, whereas an N–O link might reasonably be expected to absorb in the region 6—7 μm [cf. $CF_3\overset{+}{N}(\overset{-}{O})$=NCF$_3$ shows an absorption at 6.37 μm[9] (N–O asymm. str.) and $CF_3\overset{+}{N}(\overset{-}{O})$=CF$_2$ absorbs at 6.69 μm[10]]. The mass spectra of compounds (1) and (2) do not show peaks due to $(M - 16)^+$ or $(M - 32)^+$ ions as would be expected if they contained $\overset{+}{N}$–O bonds.[11]

Perfluoro(4,7-dimethyl-1,3-dioxa-2-thia-4,7-diazacyclo-

CF$_2$—CF$_2$

F$_3$C—N   N—CF$_3$

O—S—O

O

CF$_2$—CF$_2$ CF$_2$—CF$_2$

F$_3$C—N   N—CF$_3$ ———→ F$_3$C—N   N—CF$_3$ + SO$_2$

O—S· ·O

O

| −CF$_3$NO | −CF$_3$NO

CF$_2$—ĊF$_2$ F$_3$C—N—CF$_2$–ĊF$_2$

F$_3$C—N   −SO$_2$→   O

O—S:

O

F$_3$C—Ṅ   + CF$_2$=CF$_2$ CF$_3$NO↗   F$_3$C—N——CF$_2$

O—S·   O——CF$_2$

O

| |

CF$_3$NO + SO$_2$ F$_3$C—N=CF$_2$ + COF$_2$

Scheme.

heptane 2,2-dioxide) (1) oxidises iodide ion rapidly and quantitatively [1 mole (1) ——→ 1 mole I$_2$] in aqueous acetone at room temperature, but, like its linear analogue (3), it is stable to hydrolysis by water and by aqueous potassium hydroxide at 110—120 °C. It is also stable to prolonged u.v. irradiation, its u.v. spectrum showing no absorptions in the region 200—350 nm. Flow pyrolysis at 350 °C and ca. 1 mmHg pressure in platinum gives trifluoronitrosomethane, trifluoromethyl isocyanate, carbonyl fluoride, perfluoro(N-methylenemethylamine), perfluoro(2-methyl-1,2-oxazetidine), and sulphur dioxide, together with unidentified materials. The identified products can be accounted for by assuming that, as in the pyrolysis of compound (3), the S–O bond(s) break first (see Scheme). [Adventitious hydrolysis of perfluoro(N-methylenemethylamine) would account for the presence of trifluoromethyl isocyanate in the pyrolysis products.] Observation of the purple dioxyl in the pyrolysis collecting traps supports this mechanism. Failure to isolate the dioxyl from the products is attributed to reaction with tap grease; it has been shown that (CF$_3$)$_2$NO reacts very rapidly with hydrocarbons.[12]

Perfluoro(4,7-dimethyl-1,3-dioxa-2-thia-4,7-diazacycloheptane 2,2-dioxide) (1) reacts slowly with triphenylphosphine at room temperature giving perfluoro(3,6-dimethyl-1-oxa-2-thia-3,6-diazacyclohexane 2,2-dioxide) (5), perfluoro(2,5-dimethyl-1-thia-2,5-diazacyclopentane 1,1-dioxide) (6), and triphenylphosphine oxide. The recovery of compound (1) as unchanged material and as products (5) and (6), ranged from ca. 50 to ca. 85%, indicating that further reactions of the products with triphenylphosphine occurred giving involatile products. From the results of five experiments, no systematic variation of conversion with reaction time (4—28 days) or molar ratio of Ph$_3$P to (1) used (ca. 1:1 to ca. 11:1) could be discerned. The volatile materials from a reaction carried out at 100 °C contained sulphur dioxide in addition to the cyclopentane (6).

The structures proposed for the products (5) and (6) are based on spectroscopic evidence. The i.r. spectra show strong absorptions corresponding to a –SO$_2$– asymmetric stretch [6.79 μm (5), 6.93 μm (6); cf. 6.73 μm (1), 6.68 μm (3),[7] and 6.70 μm (4)] and no other absorptions at wavelengths below 7 μm. Comparison of the ^{19}F n.m.r. spectra of compounds (5) and (6) with those of (1), (3), and (4) indicates the presence of both CF$_2$N(CF$_3$)OSO$_2$ and CF$_2$N(CF$_3$)SO$_2$ groupings in (5) and only the latter grouping in (6). The mass spectra of compounds (1), (5), and (6) show significant differences which correlate with the structures proposed. The ions (M^+ − SO$_2$) are observed in the spectra of compounds (1) and (5) but not in that of (6). The loss of SO$_2$ from the cyclopentane (6) would give a product which would be expected to break down rapidly to give (C$_2$F$_5$N)$^+$, and the intensity of this signal is indeed much greater in the mass spectrum of (6) than in those of (1) and (5); this leads to a much lower intensity of (C$_2$F$_4$)$^+$ in the spectrum of (6) than in those of (1) and (5). The intensities of the ions m/z 199 (C$_3$F$_7$NO)$^+$ and m/z 99 (CF$_3$NO)$^+$ are much greater in the mass spectra of compounds (1) and (5) which contain the grouping CF$_2$CF$_2$N(CF$_3$)O than in that of (6) which does not. The ion m/z 197 (C$_2$F$_5$NSO$_2$)$^+$ is abundant in the spectrum of compound (6) but not in those of (1) and (5).

Experimental

I.r. spectra were recorded using Perkin-Elmer 137 and 257 spectrometers, n.m.r. spectra with a Perkin-Elmer R10, Perkin-Elmer-Hitachi R20 (^{19}F at 56.46 MHz) or Varian HA-100 (^{19}F at 94.12 MHz) spectrometer, and mass spectra with an A.E.I. MS902 spectrometer. ^{19}F Chemical shifts (δ_F) are quoted with reference to external CF$_3$CO$_2$H, values to high field being designated positive. G.l.c. analyses were carried out using either a Pye 104 instrument fitted with a flame ionisation detector or a Perkin-Elmer model 451 instrument. A specially adapted Pye 104 chromatograph was used for preparative separations. The molecular weights of volatile compounds were determined using Regnault's method. Reactants and products were manipulated in a conventional vacuum system to avoid contamination and toxicity hazards. Nitroxides were stored in a section of the apparatus fitted with 'Teflon' 'Rotaflo' taps. The dioxyl,[2] bis(trifluoromethyl) nitroxide,[13] and perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane)[3] were prepared using methods described in the literature.

Reactions of Perfluoro-2,5-diazahexane 2,5-Dioxyl.—(a) *With sulphur dioxide.* The dioxyl (4.31 g, 14.46 mmol) and sulphur dioxide (1.02 g, 15.92 mmol) were successively condensed, in vacuo, into a cold (−196 °C) Pyrex tube (20 cm^3), which was then sealed and allowed to warm to room temperature. Within 1 h the reaction mixture became colourless and the tube was warm. Trap-to-trap fractional condensation of the product, in vacuo, gave sulphur dioxide (0.12 g, 1.87 mmol) and (−23 °C trap) perfluoro(4,7-dimethyl-1,3-dioxa-2-thia-4,7-diazacycloheptane 2,2-dioxide) (1) (5.01 g, 13.84 mmol, 96%), a colourless liquid, b.p. 114 °C at 760 mmHg (isoteniscope) (Found: C, 13.4; F, 52.3; N, 7.7. C$_4$F$_{10}$N$_2$O$_4$S requires C, 13.3; F, 52.5 N, 7.7%); showing no absorptions in the range 200—350 nm; λ$_{max.}$ (vapour) 6.73s, 7.41s, 7.72vs, 7.93vs, 8.07vs, 8.28s, 8.42s, 9.17m, 9.36vw, 9.88s, 10.99s, 11.62s, 12.00s, 12.56s, 12.90s, 13.95s, and 14.26m μm; δ$_F$ (pure liquid, 35 °C) −12.5 (6 F, m, CF$_3$) and an AB-type multiplet showing further splitting, centred at 35.9 (4 F, J$_{AB}$ ca. 205 Hz, CF$_2$); m/z 343 (3.8%, M^+ − F), 298 (1.9, M^+ − SO$_2$), 199 (62.9), 197 (0.8), 133 (11.8), 100 (54.7), 99 (33.7), and 69 (100).

A very small amount of an unidentified, involatile material remained in the reaction tube; m/z 640 (0.4%, highest mass peak observed), 199 (5.0), 133 (5.5), 100 (4.6), 99 (2.5), and 69 (100).

(*b*) *With sulphur tetrafluoride*. The dioxyl (2.65 g, 8.89 mmol) and sulphur tetrafluoride (1.13 g, 10.46 mmol) were condensed successively, *in vacuo*, into a cold ($-196\ ^\circ$ C) Pyrex tube (60 cm^3) which was then sealed and placed in a Dewar vessel containing solid CO$_2$–methylated spirits. After 1 day this bath had warmed to room temperature and the reaction mixture was colourless. Trap-to-trap fractional condensation of the product, *in vacuo*, gave a colourless gas (2.51 mmol) shown by i.r. spectroscopy and molecular weight determination (*M* 107) to be sulphur tetrafluoride (requires *M* 108) contaminated by a small amount of trifluoronitrosomethane, and ($-46\ ^\circ$ C trap) *perfluoro*(4,7-*dimethyl*-1,3-*dioxa*-2-*tetrafluorothia*-4,7-*diazacycloheptane*) (**2**) (3.15 g, 7.76 mmol, 87%), a colourless liquid (Found: C, 12.1; F, 65.5; N, 6.7. C$_4$F$_{14}$N$_2$O$_2$S requires C, 11.8; F, 65.5; N, 6.9%); $\lambda_{max.}$ (vapour) 7.32s, 7.72vs, 7.92vs, 8.08vs, 8.24s, 8.40vs, 9.14m, 9.45s, 10.82vs, 10.99sh, 11.36s, 11.49vs, 12.58w, 13.89s, and 14.18m µm; δ_F (pure liquid in capillary, 35 $^\circ$ C) -139 (2 F, t, *J ca.* 150 Hz, S–F axial[14,15]), -116.5 (2 F, t, *J ca.* 150 Hz, S–F equatorial[14,15]), -13.0 (6 F, m, CF$_3$), and an AB-type multiplet showing further splitting, centred at 35.8 (4 F, J_{AB} *ca.* 195 Hz, CF$_2$); *m/z* 225 (1.2%), 199 (7.4), 133 (10.9), 108 (1.0), 99 (5.7), 89 (41.6), 70 (19.2), and 69 (100).

Reaction of Bis(trifluoromethyl) Nitroxide with Sulphur Dioxide.—Bis(trifluoromethyl) nitroxide (0.64 g, 3.81 mmol) and sulphur dioxide (0.32 g, 5.00 mmol) were condensed successively, *in vacuo*, into a cold ($-196\ ^\circ$ C) Pyrex tube (10 cm^3) which was then sealed and allowed to warm to room temperature. After 3 days the reaction mixture had become colourless. Trap-to-trap fractional condensation of the products, *in vacuo*, gave a colourless gas (0.19 g, 2.97 mmol) identified by its i.r. spectrum as sulphur dioxide, and ($-46\ ^\circ$ C trap) perfluoro(2,6-dimethyl-3,5-dioxa-4-thia-2,6-diazaheptane 4,4-dioxide) (**3**) (0.74 g, 1.85 mmol, 97%) (Found: C, 12.4; F, 56.6; N, 7.0. Calc. for C$_4$F$_{12}$N$_2$O$_4$S: C, 12.0; F, 57.0; N, 7.0%); i.r. spectrum identical with that reported;[7] δ_F (pure liquid, 35 $^\circ$ C) -9.0 (s, CF$_3$); *m/z* 381 (0.8%, *M*$^+$ $-$ F), 168 (57.5), and 69 (100).

Reaction of Perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) with Sulphur Dioxide.—Perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) (1.38 g, 4.31 mmol) and sulphur dioxide (0.32 g, 5.00 mmol) were condensed successively, *in vacuo*, into a cold ($-196\ ^\circ$ C) Pyrex tube (10 cm^3) which was then sealed. The liquid reactants were immiscible at room temperature and no reaction had apparently taken place after 10 days on a shaker. After 15 h in a thermostat at 70 $^\circ$ C, however, the mixture had become homogeneous. Trap-to-trap fractional condensation of the products, *in vacuo*, gave a colourless gas (1.32 mmol) (*M* 67.5) shown by i.r. spectroscopy to be sulphur dioxide containing a small amount of impurity, perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) (0.42 g, 1.31 mmol, 30% recovery), and a colourless liquid ($-46\ ^\circ$ C trap) (1.15 g) shown by g.l.c. (2 m SE-30) to be a two-component mixture; the major component (*ca.* 96%), isolated by preparative-scale g.l.c. (4 m SE-30), was *perfluoro*(2,5-*dimethyl*-3-*oxa*-4-*thia*-2,5-*diazahexane* 4,4-*dioxide*) (**4**) (Found: C, 12.5; F, 59.4; N, 7.6. C$_4$F$_{12}$N$_2$O$_3$S requires C, 12.5; F, 59.4; N, 7.3%); $\lambda_{max.}$ (vapour) 6.70s, 6.75sh, 7.49sh, 7.56vs, 7.86vs, 7.97vs, 8.07vs, 8.15s, 8.25m, 8.46s, 8.59m, 9.82m, 9.93m, 10.13m, 10.31m, 12.52m, 12.90w, 13.75m, 13.93m, 15.15w, and 15.87m µm; δ_F (pure liquid in capillary, 35 $^\circ$ C) -24.0 (3 F, s, F_3CNS) and -10.0 (3 F, s, F$_3$CNO); *m/z* 365 (1.8%, *M*$^+$ $-$F), 216 (32.7), 168 (29.4), and 69 (100).

Flow Pyrolysis of Perfluoro(2,6-dimethyl-3,5-dioxa-4-thia-2,6-diazaheptane 4,4-Dioxide) (**3**).—Perfluoro(2,6-dimethyl-3,5-dioxa-4-thia-2,6-diazaheptane 4,4-dioxide) (**3**) (0.64 g, 1.60 mmol) vapour was passed at *ca.* 1 mmHg pressure through a platinum

tube (85 × 1.6 cm) heated to 350 $^\circ$ C over 70 cm of its length and connected to the vacuum system *via* cold ($-196\ ^\circ$ C) traps. The condensate was subjected to trap-to-trap fractional condensation, *in vacuo*, giving starting material (0.044 g, 0.11 mmol) and ($-120\ ^\circ$ C trap) a purple gas (4.49 mmol), the i.r. spectrum of which showed absorptions due to sulphur dioxide and bis(trifluoromethyl) nitroxide. The gas was condensed into a Pyrex tube (10 cm^3) which was then sealed under vacuum and left at room temperature for 3 days; the i.r. spectrum of the colourless liquid product (0.54 g) was identical with that of perfluoro(2,6-dimethyl-3,5-dioxa-4-thia-2,6-diazaheptane 4,4-dioxide) (**3**). In another experiment carried out under the same conditions, fractional condensation of the products from the pyrolysis of (**3**) (0.60 g, 1.50 mmol) gave starting material (0.16 g, 0.40 mmol) and the purple gas (3.20 mmol). The gas was condensed into an evacuated Pyrex tube containing tetrachloroethene (0.40 g, 2.41 mmol) which rapidly forms an involatile 1:2 adduct with bis(trifluoromethyl) nitroxide.[16] The sealed tube was left overnight at room temperature. Trap-to-trap fractional condensation of the colourless product gave a colourless gas (0.07 g, 1.09 mmol) shown by i.r. spectroscopy to be sulphur dioxide containing traces of impurities, an excess of tetrachloroethene, and a colourless involatile liquid having an i.r. spectrum identical with that of the adduct made in a separate reaction of the nitroxide with the olefin.

Reactions of Perfluoro(4,7-dimethyl-1,3-dioxa-2-thia-4,7-diazacycloheptane 2,2-Dioxide.—(*a*) *With iodide ion*. Perfluoro-(4,7-dimethyl-1,3-dioxa-2-thia-4,7-diazacycloheptane 2,2-dioxide) (0.63 g, 1.74 mmol) was shaken in a sealed evacuated tube with potassium iodide (2.0 g, 12.0 mmol) in the presence of acetone (3 cm^3) containing *ca.* 10% water for 2 days at room temperature in darkness. The iodine liberated [1.72 mmol, 98.9% based on CF$_3$N$\underline{CF_2CF_2N(CF_3)OSO_2O} \equiv 1$ I$_2$] was estimated by standard volumetric techniques using aqueous sodium thiosulphate.

(*b*) *Attempted hydrolysis*. The cyclic adduct (1.20 g, 3.31 mmol) and water (*ca.* 5 cm^3) were sealed, *in vacuo*, in a Pyrex tube (20 cm^3) and heated in an oven at 110—120 $^\circ$ C for 60 days. The products were taken into the vacuum system *via* a column of phosphorus pentaoxide and 96% of the cyclic adduct was recovered. The cyclic adduct (1.45 g, 4.00 mmol, 97%) was similarly recovered after 1.49 g (4.11 mmol) had been heated for 48 h at 110—120 $^\circ$ C in a sealed evacuated Pyrex tube (20 cm^3) with 10% aqueous potassium hydroxide (10 cm^3, w/v).

(*c*) *Attempted photolysis*. Perfluoro(4,7-dimethyl-1,3-dioxa-2-thia-4,7-diazacycloheptane 2,2-dioxide) (1.70 g, 4.70 mmol) contained in a sealed, evacuated silica tube (250 cm^3), the lower 10 cm of which was covered with black tape, was irradiated for 560 h with u.v. radiation from a Hanovia S500 lamp at a distance of 30 cm. Starting material (1.65 g, 4.55 mmol, 97%) was recovered. To exclude the possibility that photolysis had occurred giving the dioxyl and sulphur dioxide which subsequently recombined, the cyclic adduct (0.40 g, 1.10 mmol) was irradiated for 60 h under the same conditions in the presence of tetrachloroethene (0.40 g, 2.41 mmol) which reacts with the dioxyl to form a 1:1 copolymer;[17] 0.39 g (98%) of the cyclic adduct was recovered.

(*d*) *Flow pyrolysis*. Perfluoro(4,7-dimethyl-1,3-dioxa-2-thia-4,7-diazacycloheptane 2,2-dioxide) (0.55 g, 1.52 mmol) vapour was passed at *ca.* 1 mmHg pressure through a platinum tube (85 × 1.6 cm) heated to 350 $^\circ$ C over 70 cm of its length and connected to the vacuum system *via* cold (-78 and $-196\ ^\circ$ C) traps. Although the freshly condensed material in the $-78\ ^\circ$ C trap was slightly purple in colour indicating the presence of dioxyl, only starting material (0.14 g, 0.39 mmol) was isolated on work-up. Fractional condensation, *in vacuo*, of the products collected in the $-196\ ^\circ$ C trap gave ($-96\ ^\circ$ C trap) a colourless

unidentified gas (0.15 mmol) (λ_{max}. 5.25, 5.50, 5.71, 6.77, 7.29, 7.75—8.10, 8.21, 9.42, 9.73, 10.30, and 13.9 µm); (− 120 °C trap) a colourless gas (1.22 mmol) shown by coupled g.l.c.–i.r. (10 m SE-30) and coupled g.l.c.–mass spectroscopy (4.5 m SE-30) to *contain sulphur* dioxide (0.64 mmol), perfluoro(2-methyl-1,2-oxazetidine) (0.29 mmol), and two unidentified components (0.09 and 0.20 mmol); (− 140 °C trap) a colourless gas (0.39 mmol) shown by i.r. spectroscopy and coupled g.l.c.–mass spectroscopy (4 m SE-30) to be perfluoro(N-methylenemethyl-amine) containing traces of sulphur dioxide and perfluoro(2-methyl-1,2-oxazetidine); and (− 196 °C trap) a gas (1.18 mmol) with a faint blue colour shown by coupled g.l.c.–i.r. (10 m SE-30) and coupled g.l.c.–mass spectroscopy (4.5 m SE-30) to contain trifluoronitrosomethane (0.39 mmol), carbonyl fluoride (0.55 mmol), trifluoromethyl isocyanate (0.20 mmol), traces of perfluoro(N-methylenemethylamine), and an unidentified component (0.04 mmol).

(*e*) *With triphenylphosphine*. (i) *At* 100 °C. Perfluoro(4,7-dimethyl-1,3-dioxa-2-thia-4,7-diazacycloheptane 2,2-dioxide) (1.50 g, 4.14 mmol) was condensed, *in vacuo*, into a cold (− 196 °C) Pyrex tube (30 cm³) containing triphenylphosphine (6.00 g, 22.88 mmol). The tube was sealed and left in an oven at 100 °C for 8 h. Trap-to-trap fractional condensation of the volatile products, *in vacuo*, gave sulphur dioxide (0.15 mmol) and (− 46 and − 78 °C traps) *perfluoro*(2,5-*dimethyl*-1-*thia*-2,5-*diazacyclopentane* 1,1-*dioxide*) (6) (0.24 g, 0.73 mmol, 17%) (Found: C, 15.0; F, 57.4; N, 8.4. $C_4F_{10}N_2O_2S$ requires C, 14.6; F, 57.6; N, 8.5%), a colourless liquid; λ_{max}. (vapour) 6.93s, 7.01sh, 7.24m, 7.55vs, 8.10vs, 8.51s, 9.01m, 9.95w, 10.73m, 11.49w, and 13.62w µm; δ_F (pure liquid in capillary, 35 °C) − 22.5 (6 F, t, *J* *ca*. 8 Hz, CF_3) and 17.5 (4 F, q, *J* *ca*. 8 Hz, CF_2); *m/z* 330 (0.4%, M^+), 311 (2.3), 199 (3.6), 197 (22.6), 133 (54.7), 100 (4.3), 99 (0.7), and 69 (100).

(ii) *At room temperature*. Perfluoro(4,7-dimethyl-1,3-dioxa-2-thia-4,7-diazacycloheptane 2,2-dioxide) (1.45 g, 4.00 mmol) was condensed, *in vacuo*, into a cold (− 196 °C) Pyrex tube (30 cm³) containing triphenylphosphine (1.00 g, 3.81 mmol). The sealed tube was left in darkness at room temperature for 12 days. The volatile products (1.20 g) were taken into a trap at − 196 °C and identified by coupled g.l.c.–mass spectrometry (4 m SE-30) as a mixture of perfluoro(2,5-dimethyl-1-thia-2,5-diazacyclo-pentane 1,1-dioxide) (0.12 mmol, 3%), cyclic starting material (2.01 mmol, 50%), and *perfluoro*(3,6-*dimethyl*-1-*oxa*-2-*thia*-3,6-*diazacyclohexane* 2,2-*dioxide*) (5) (1.23 mmol, 31%), a colourless liquid isolated by preparative-scale g.l.c. (4 m SE-30) (Found: C, 14.1; F, 54.7; N, 8.4. $C_4F_{10}N_2O_3S$ requires C, 13.9; F, 54.9; N, 8.1%); λ_{max}. (vapour) 6.79s, 6.88sh, 7.39s, 7.72vs, 7.95vs, 8.16vs, 8.47vs, 9.11m, 9.76m, 10.89m, 11.30s, 12.12sh, 12.30m, 13.64m, 13.91m, and 15.27m µm; δ_F (pure liquid in capillary, 35 °C) − 24.5 (3 F, t, *J* *ca*. 11.8 Hz, $SNCF_3$), − 9.5 (3 F, t, *J* *ca*. 8.9 Hz, $ONCF_3$), 16.0 (2 F, s, CF_2), and 26.8 (2 F, d, *J* *ca*. 9.0 Hz, CF_2); *m/z* 346 (7.2%, M^+), 327 (5.5), 282 (1.7), 199 (25.3), 197 (0.0), 133 (11.8), 100 (39.1), 99 (14.5), and 69 (100). The involatile residue from the reaction was extracted with boiling light

petroleum (b.p. 100—120 °C). The filtrate was cooled and triphenylphosphine oxide, identified by its m.p., mixed m.p., and mass spectrum, crystallised out.

The results of other experiments carried out at room temperature were as follows [mmol (1), mmol Ph$_3$P, reaction time/days, mmol (1) recovered, mmol (5) isolated, mmol (6) isolated] 2.79, 9.57, 4, 1.49, 0.32, and 0.02; 3.53, 5.00, 21, 1.37, 0.55, and 0.04; 2.32, 3.82, 22, 1.03, 0.40, and 0.015; 3.31, 38.2, 28, 1.90, 0.30, and trace amount.

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