315. *Perfluoroalkyl Derivatives of Nitrogen. Part XIII.*[1] *Tristrifluoromethylhydroxylamine*

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Tristrifluoromethylhydroxylamine, prepared by the irradiation of trifluoronitrosomethane and trifluoroiodomethane, photolyses to give $(CF_3)_2N\cdot$ radicals and thence, by dimerisation, perfluorotetramethylhydrazine. Pyrolysis of the compounds $(CF_3)_2N{\cdot}O{\cdot}CF_3$, $(CF_3)_2NF$, and $(CF_3)_2N{\cdot}O{\cdot}NO$ at 730—775° is also considered to give $(CF_3)_2N\cdot$ radicals which mainly disproportionate to the compounds $CF_3{\cdot}N{:}CF_2$ and $(CF_3)_2NF$.

The reversible dimerisation of the deep blue gas trifluoronitrosomethane to its dimer, *O*-nitrosobistrifluoromethylhydroxylamine, and the rearrangement of the latter into bistrifluoromethylnitramine are considered to involve free radicals as intermediates, *e.g.*,[1,2]

$$CF_3NO \xrightarrow{\text{u.v.}} NO + CF_3\cdot \xrightarrow{CF_3NO} (CF_3)_2N{\cdot}O\cdot \xrightarrow{NO} (CF_3)_2N{\cdot}O{\cdot}NO$$

Irradiation of trifluoroiodomethane in the presence of trifluoronitrosomethane enables the initial attack of a trifluoromethyl radical on the nitrogen of trifluoronitrosomethane to be followed by combination with a trifluoromethyl radical:

$$CF_3I \xrightarrow{\text{u.v.}} CF_3\cdot \xrightarrow{CF_3NO} (CF_3)_2N{\cdot}O\cdot \xrightarrow{CF_3\cdot} (CF_3)_2N{\cdot}O{\cdot}CF_3$$

Free-radical addition to the N=O of a nitroso-compound has been postulated earlier, *e.g.*, addition of nitric oxide[3] and of aryl radicals.[4]

Tristrifluoromethylhydroxylamine, thus prepared in 49% yield and 42% conversion, is separated from *O*-nitrosobistrifluoromethylhydroxylamine by hydrolysis of the latter.[2] Its infrared spectrum contains strong bands in the 7·55—8·45 μ region (C–F stretching vibrations), at 9·38 μ (N–O stretching vibration), 10·29, 10·31 doublet (C–N stretching vibration) (cf. 10·6 μ for the N–O band and 10·9 μ for the C–N band in trimethylhydroxylamine[5]), weaker bands at 11·17 and 12·10 μ (C–N–C bending vibrations), and a strong band at 14·03 μ (CF_3 deformation). The 60 Mc./sec. ^{19}F n.m.r. spectrum showed two regions of absorption, at 8·1 and 10·0 p.p.m. to low field from external reference trifluoroacetic acid. The lower-field band was a 1 : 6 : 15 : 20 : 15 : 6 : 1 septet (total integrated intensity 1) and was assigned to the $CF_3{\cdot}O$ group, whilst the higher-field band was a 1 : 3 : 3 : 1 quartet (total integrated intensity 2), and was associated with the $(CF_3)_2N$ group. The coupling constant between the fluorines in different environments was 5·2 c./sec. Tristrifluoromethylhydroxylamine shows no maxima or inflections in its ultraviolet spectrum (vapour); general absorption starts at about 250 mμ and increases with decreasing wavelength (ε 6·4 at 200 mμ).

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[1] Part XII, preceding Paper.

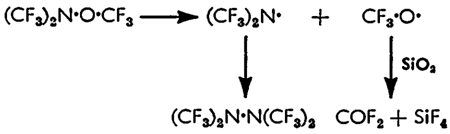
[2] Jander and Haszeldine, *J.*, 1954, 912; Haszeldine and Mattinson, *J.*, 1957, 1741.

[3] Birchall, Bloom, Haszeldine, and Willis, *Proc. Chem. Soc.*, 1959, 367; *J.*, 1962, 3021; Christie, *Proc. Roy. Soc.*, 1959, *A*, **249**, 258.

[4] Gingras and Waters, *J.*, 1954, 1920; Boyd, Souther, and Waters, *J.*, 1958, 2056.

[5] Davies and Spiers, *J.*, 1959, 3971.

Prolonged irradiation of tristrifluoromethylhydroxylamine gives perfluorotetramethylhydrazine in high yield and breakdown products



Tristrifluoromethylhydroxylamine contains the $-CF_2{\cdot}N(CF_3){\cdot}O{\cdot}CF_2-$ unit found in the copolymer and in the oxazetidine obtained by reaction of trifluoronitrosomethane with tetrafluoroethylene,[6] and like the copolymer and the oxazetidine it is markedly resistant to attack by hot concentrated acid or aqueous alkali. Pyrolysis of tristrifluoromethylhydroxylamine requires a higher temperature than for the polymer or the oxazetidine, probably since the last two can degrade to stable compounds ($CF_3{\cdot}N{:}CF_2$ and COF_2) by a low-energy path.[6] Pyrolysis of the hydroxylamine is essentially complete at 775° to give approximately equimolar amounts of perfluoro(methylenemethylamine) (39% yield) and heptafluorodimethylamine (35% yield), together with carbonyl fluoride and silicon tetrafluoride:

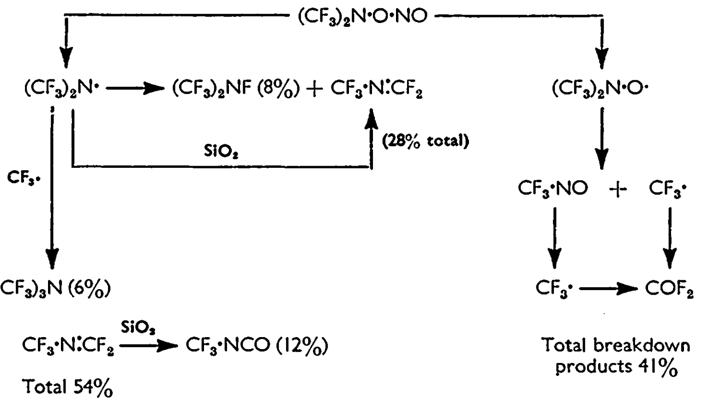
$$(CF_3)_2N{\cdot}O{\cdot}CF_3 \longrightarrow (CF_3)_2N{\cdot} + CF_3{\cdot}O{\cdot}$$
$$2(CF_3)_2N{\cdot} \longrightarrow (CF_3)_2NF + CF_3{\cdot}N{:}CF_2$$

The $(CF_3)_2N{\cdot}$ radicals disproportionate under these conditions rather than dimerise as in the photochemical reaction. Small quantities of carbon tetrafluoride and hexafluoroethane are also formed.

Heptafluorodimethylamine is itself only 22% decomposed under these conditions:

$$(CF_3)_2NF \longrightarrow (CF_3)_2N{\cdot} \xrightarrow{SiO_2} CF_3{\cdot}N{:}CF_2 \quad (77\%\ \text{yield}) \quad (+SiF_4)$$
$$CF_3{\cdot}N{:}CF_2 \xrightarrow{SiO_2} CF_3{\cdot}NCO \quad (9\%\ \text{yield}) \quad (+SiF_4)$$

The pyrolysis products of *O*-nitrosobistrifluoromethylhydroxylamine at 730° can also be interpreted by formation of the $(CF_3)_2N{\cdot}$ and $(CF_3)_2N{\cdot}O{\cdot}$ radicals (yields in parentheses):



The yield of 54% for the CF_3–N compounds $(CF_3)_2NF$, $CF_3{\cdot}N{:}CF_2$, $(CF_3)_3N$, and $CF_3{\cdot}NCO$ from the complete decomposition of *O*-nitrosobistrifluoromethylhydroxylamine must be corrected for the fact that $(CF_3)_2N{\cdot}$ radicals also break down to give carbonyl fluoride and silicon tetrafluoride. If it is assumed that the above reported complete pyrolysis of tristrifluoromethylhydroxylamine under similar conditions involved N–O and not O–C fission in the initial step, then it is known that, of the $(CF_3)_2N{\cdot}$ radicals so formed, only

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[6] Barr and Haszeldine, *J.*, 1955, 1881 *et seq.*

74% appear as CF_3–N compounds [$CF_3\cdot N{:}CF_2$ (39%) plus $(CF_3)_2NF$ (35%)] and 26% appear as breakdown products. The total yield of 54% for the CF_3–N compounds obtained from *O*-nitrosobistrifluoromethylhydroxylamine is thus equivalent to a yield of 73% of $(CF_3)_2N\cdot$ radicals, *i.e.*, $(CF_3)_2N$–O fission has occurred to the extent of 73% and, by difference, $(CF_3)_2N\cdot O$–N fission, which leads only to breakdown products, must have occurred to the extent of 27% during the pyrolysis of *O*-nitrosobistrifluoromethylhydroxylamine.

Since the above results with tristrifluoromethylhydroxylamine were obtained, the compound has been mentioned briefly in a Note,[7] but without any experimental detail.

EXPERIMENTAL

Irradiation of Trifluoronitrosomethane with Trifluoroiodomethane.—(*a*) *Under pressure.* Trifluoronitrosomethane (2·12 g., 21·4 mmoles), trifluoroiodomethane (4·16 g., 21·2 mmoles), and mercury (8 ml.) were sealed in a 290 ml. silica tube and irradiated, with shaking, by a Hanovia S250 lamp for 7 days. The walls of the tube became coated with mercuric iodide, which was periodically dislodged by sublimation to the lower end cooled in liquid nitrogen. Distillation, gas chromatography, molecular-weight determination, and infrared spectroscopy showed the products to be nitrogen (10 ml.), carbon dioxide (4%), recovered trifluoronitrosomethane (0·136 g., 1·37 mmoles; 6%), tristrifluoromethylhydroxylamine (2·30 g., 9·7 mmoles; 48% yield) (*M*, 237), *O*-nitrosobistrifluoromethylhydroxylamine (0·180 g., 0·91 mmole; 9% yield), and higher-boiling material (1·160 g., 18% conversion) (*M*, *ca.* 350). The residual solid in the tube smelt strongly of trifluoromethylmercuric iodide, and showed an increase in weight of 1·8 g. over the mercury used.

A similar reaction using a 2 : 1 molar ratio of $CF_3NO{:}CF_3I$ gave the *O*-nitroso-dimer (1·19 g., 6·0 mmoles; 42% yield), tristrifluoromethylhydroxylamine (1·21 g., 5·1 mmoles; 18% yield), higher-boiling material (25% yield). The composition of these fractions of higher b. p. will be discussed in a later publication.

(*b*) *Under reduced pressure.* Irradiation by a Hanovia S250 lamp of trifluoronitrosomethane (2·91 g., 29·4 mmoles) and trifluoroiodomethane (5·88 g., 30·0 mmoles) in the presence of mercury in a silica flask at a pressure of 500 mm. for 4 days gave trifluoronitrosomethane (0·141 g., 1·43 mmoles, 5% yield), *O*-nitrosobistrifluoromethylhydroxylamine (0·662 g., 3·27 mmoles; 23% yield), tristrifluoromethylhydroxylamine (3·155 g., 13·4 mmoles; 48% yield), and higher-boiling material (0·302 g., 3% conversion) (*M*, *ca.* 300).

In a second experiment, in the absence of mercury, trifluoronitrosomethane (27·4 g., 0·277 mole) and trifluoroiodomethane (54·4 g., 0·277 mole) were expanded into a 20 l., 500w photochemical reactor [1] (pressure 521 mm. at 20°), and irradiated for 7·5 hr., when very little blue colour remained, and the pressure had fallen to 265 mm. at 40°. The products were: carbon dioxide, carbonyl fluoride, and silicon tetrafluoride (0·64 g., 0·0107 mole), trifluoronitrosomethane (3·75 g., 0·0379 mole; 14% recovery), trifluoroiodomethane (5·15 g., 0·0263 mole; 10% recovery), *O*-nitrosobistrifluoromethylhydroxylamine (11·66 g., 0·0589 mole; 50% yield), tristrifluoromethylhydroxylamine (27·60 g., 0·116 mole; 49% yield). Little higher-boiling material was recovered; the iodine deposited on the cooler surfaces of the bulb was dissolved in a known weight of acetone, giving an increase in weight of 32 g. (Calc. for CF_3I decomposed: 31·9 g.).

Tristrifluoromethylhydroxylamine.—(*a*) *Purification.* Tristrifluoromethylhydroxylamine was separated from *O*-nitrosobistrifluoromethylhydroxylamine by hydrolysis of the latter to *NN*-bistrifluoromethylhydroxylamine.[1,2] The mixture [7·68 g., 33·2 mmoles; *M*, 231·5; shown by gas–liquid chromatography to contain 86% $(CF_3)_2N\cdot O\cdot CF_3$ and 14% $(CF_3)_2N\cdot O\cdot NO$], sealed in a 100 ml. Pyrex tube with mercury (13 g.) and 50% v/v aqueous hydrochloric acid (3·4 ml.), and shaken for 14 hr. at 20°, gave tristrifluoromethylhydroxylamine (6·64 g., 28·1 mmoles; *M*, 236) and *NN*-bistrifluoromethylhydroxylamine (0·81 g., 4·8 mmoles; *M*, 169), corresponding to a composition for the original mixture of $(CF_3)_2N\cdot O\cdot CF_3$ 85%, $(CF_3)_2N\cdot O\cdot NO$ 14%. Gas–liquid chromatography revealed 2% of impurity in the tristrifluoromethylhydroxylamine, and final purification was achieved on a 5 m. 30% dinonyl phthalate–Celite column to give >99·9% pure *tristrifluoromethylhydroxylamine* (Found: C, 15·3; N, 6·0%; *M*, 237. C_3F_9NO requires C, 15·2; N, 5·9%; *M*, 237). Its vapour pressure, measured over the range −47 to −5°, is given

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[7] Yakubovich, Makarov, Ginsburg, Privezentseva, and Martynova, *Doklady Akad. Nauk. S.S.S.R.*, 1961, 141, 125.

by the equation $\log_{10} p$ (mm.) = 8·032 − 1410/T, whence the b. p. is calculated as 0·6°, the latent heat of vaporisation as 6455 cal. mole^{-1}, and Trouton's constant as 23·6.

(*b*) *Stability to acid or aqueous base.* Tristrifluoromethylhydroxylamine (1·0 g.) was recovered unchanged when sealed in a 30 ml. Carius tube with either concentrated hydrochloric acid (3 ml.), or 30% aqueous sodium hydroxide (2 ml.), and heated to 100° for 16 hr.

(*c*) *Photolysis.* Tristrifluoromethylhydroxylamine (8·87 g., 37·5 mmole) in a vertical 360 ml. silica tube with the lower two inches blacked out to prevent irradiation of liquid products, and exposed to a Hanovia S500 lamp for 12 days, gave carbonyl fluoride and silicon tetrafluoride (2·698 g., 36·76 mmoles) (*M*, 73·5), tristrifluoromethylhydroxylamine (3·91 g., 16·5 mmoles; 44% recovery) (*M*, 237), and higher-boiling material (3·15 g.; *M*, 302). Redistillation of the last fraction through a packed column gave perfluorotetramethylhydrazine (2·19 g., 9·77 mmoles; 93% yield) (Found: C, 15·6; N, 9·0%; *M*, 306. Calc. for $C_4F_{12}N_2$: C, 15·8; N, 9·2%; *M*, 304), b. p. 31—32° (lit.,[8] 32°) identified by means of its infrared spectrum, which revealed the presence of a small quantity of a compound later identified as $(CF_3)_2N{\cdot}O{\cdot}N(CF_3)_2$.[9]

(*d*) *Pyrolysis.* Tristrifluoromethylhydroxylamine was recovered unchanged after being heated for 2·5 days at 205°, and also after being passed at 1—2 mm. pressure through an 8 mm. silica tube heated to 500° over 55 cm. of its length. The hydroxylamine (1·44 g., 6·06 mmoles) was passed through the silica pyrolysis tube at 775° at a rate of 5—6 ml. vapour/min. at 2—3 mm., to give condensable products initially separated into (i) a fraction (88 ml.; *M*, 141) condensing at −135°, shown by infrared analysis to contain mainly perfluoro(methylenemethylamine) contaminated by dinitrogen tetroxide and heptafluorodimethylamine, and (ii) a fraction (240 ml.; *M*, 102) condensing at −196°, containing mainly carbonyl fluoride, together with silicon tetrafluoride, carbon tetrafluoride, and heptafluorodimethylamine. Non-condensable gas (11 ml.) was trapped by active charcoal. Some etching of the pyrolysis tube had taken place. Dinitrogen tetroxide (0·005 g., 0·58 mmole; 19% yield) was removed by reaction with mercury, and refractionation gave perfluoro(methylenemethylamine) (0·315 g., 2·36 mmole; 39% yield), and carbonyl fluoride (both then destroyed with 50% aqueous base), carbon tetrafluoride (0·103 g., 1·00 mmole; 6% yield; *M*, 103), and heptafluorodimethylamine (0·365 g., 2·14 mmole; 35% yield) (Found: C, 14·0; N, 8·2%; *M*, 172. Calc. for C_2F_7N: C, 14·0; N, 8·2%; *M*, 171).

The infrared spectrum of heptafluorodimethylamine shows strong absorption bands at 7·64, 7·87, 8·07, 8·20, 9·65, 10·31, 14·10 μ (triplet). Its vapour pressure, measured over the range −74 to −43° satisfies the equation $\log_{10} p$ (mm.) = 7·653 − 1118/T whence the b. p. is calculated as −39·0° (lit.,[10] −37·0°), the latent heat of vaporisation as 5120 cal. mole^{-1}, and Trouton's constant as 21·9.

Pyrolysis of Heptafluorodimethylamine.—Heptafluorodimethylamine (0·370 g., 2·18 mmole), pyrolysed under the conditions described above for tristrifluoromethylhydroxylamine gave heptafluorodimethylamine (0·291 g., 1·71 mmole; 78% recovery; *M*, 170), perfluoro(methylenemethylamine) (0·048 g., 0·36 mmole; 77% yield), trifluoromethyl isocyanate (0·005 g., 0·044 mmole; 9% yield), carbonyl fluoride, and silicon tetrafluoride.

Pyrolysis of O-*Nitrosobistrifluoromethylhydroxylamine.*—This compound (1·325 g., 6·69 mmoles) pyrolysed at 730° under the conditions described for tristrifluoromethylhydroxylamine, gave perfluoro(methylenemethylamine) (0·251 g., 1·89 mmoles; 28% yield), trifluoromethyl isocyanate (0·088 g., 0·79 mmole; 12% yield), heptafluorodimethylamine (0·094 g., 0·55 mmole; 8% yield), perfluorotrimethylamine (0·088 g., 0·40 mmole; 6% yield), carbonyl fluoride and silicon tetrafluoride (0·652 g., 8·87 mmoles), and dinitrogen tetroxide and nitrous oxide (5·18 mmoles).

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[8] Dacey and Young, *J. Chem. Phys.*, 1955, **23**, 1302.
[9] Haszeldine and Tipping, unpublished results.
[10] Thompson and Emeléus, *J.*, 1949, 3080.