

314. *Perfluoroalkyl Derivatives of Nitrogen. Part XII.¹ The Reversible Photochemical Dimerisation of Trifluoronitrosomethane and Rearrangement of the O-Nitroso-dimer to Bistrifluoromethylnitramine*

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Improvements in the technique for the preparation of trifluoronitrosomethane, and an investigation of factors influencing yield and conversion, are reported. The photochemical dimerisation of trifluoronitrosomethane to give *O*-nitrosobistrifluoromethylhydroxylamine is reversible. Bistrifluoromethylnitramine, a by-product from the formation of the *O*-nitroso-dimer, and an isomer of it, is also obtained by photolysis or pyrolysis of the *O*-nitroso-dimer, or by nitration of the amine $(\text{CF}_3)_2\text{NH}$.

THE first general method reported for the preparation of a polyfluoronitrosoalkane was the free-radical reaction of the polyfluoroalkyl iodide with nitric oxide in the presence of mercury. Improvements in the technique used for the preparation of trifluoronitrosomethane² changed the 10% conversion (75% yield) after 3–7 days into a 38% conversion (85% yield) after 24 hr. Study of the reaction variables, now reported, has enabled a 57% conversion (80% yield) of trifluoroiodomethane into the nitroso-compound to be obtained after 3–4 hr., so that this compound can now be made in relatively large quantities.

The preparation of trifluoronitrosomethane. The main factors affecting the yield and conversion in the photochemical preparation of trifluoronitrosomethane are (a) initial pressure, (b) initial reactant ratio, (c) irradiation time, (d) intensity of the ultraviolet

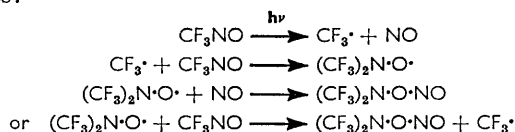
¹ Part XI, Banks, Haszeldine, and Sutcliffe, *J.*, 1964, 4066.

² Haszeldine, *J.*, 1953, 2075; Barr and Haszeldine, *J.*, 1955, 1881.

radiation, (e) reaction temperature, and (f) the method used for removal of nitric oxide from the product.

Increase in the intensity of irradiation, which also raises the reaction temperature slightly in the photochemical reactor, enables much shorter irradiation times to be employed; use of reaction temperatures $>80^\circ$ leads to extensive breakdown. Initial reaction pressures close to one atmosphere give best results, as does the use of $\text{NO} : \text{CF}_3\text{I}$ ratios of 1 : 1 to 1.5 : 1. The method of removal of unchanged nitric oxide at the end of the reaction is important, since if it is separated by fractional condensation or evaporation,³ the yield of trifluoronitrosomethane is significantly lowered by its liquid-phase reaction with nitric oxide to give trifluoronitromethane, dinitrogen tetroxide, and nitrogen; furthermore, it is not possible to remove traces of nitric oxide from the trifluoronitrosomethane by fractional condensation or evaporation, and the decomposition of trifluoronitrosomethane on storage reported by some authors is undoubtedly caused by inadequate removal of nitric oxide. The usefulness of having mercury present during and immediately after the photochemical reaction has been confirmed, since removal of unchanged nitric oxide by admission of air or oxygen and reaction of the resultant dinitrogen tetroxide with mercury yields a trifluoronitrosomethane fraction which is readily purified, and which does not decompose when kept in absence of light.

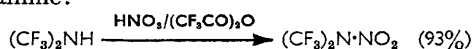
Reversible dimerisation of trifluoronitrosomethane. The dimer of trifluoronitrosomethane, *O*-nitrosobistrifluoromethylhydroxylamine, is prepared⁴ by exposure of the monomer to ultraviolet or visible light. The ultraviolet reaction probably involves radical intermediates:



It has now been established that this dimerisation is reversible, since (a) prolonged irradiation of trifluoronitrosomethane fails to increase the yield of the dimer appreciably and leads only to decomposition, and (b) irradiation of pure *O*-nitrosobistrifluoromethylhydroxylamine rapidly yields trifluoronitrosomethane. Under the particular set of conditions used, the equilibrium $(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{NO} \rightleftharpoons 2\text{CF}_3\text{NO}$ lies well to the left. Photolysis of *O*-nitrosobistrifluoromethylhydroxylamine also causes breakdown by way of $(\text{CF}_3)_2\text{N}\cdot$ radicals, leading to the formation of the compounds $\text{CF}_3\cdot\text{N}:\text{CF}_2$ and $(\text{CF}_3)_2\text{N}\cdot\text{NO}_2$ (see below).

Rearrangement of O-nitrosobistrifluoromethylhydroxylamine into bistrifluoromethylnitramine. The infrared spectra of some samples of *O*-nitrosobistrifluoromethylhydroxylamine recovered after the irradiation of the pure *O*-nitroso-compound referred to above, showed a small impurity band at 5.99μ , assigned to $>\text{N}\cdot\text{NO}$ or $>\text{N}\cdot\text{NO}_2$ groups. A compound with strong absorption in the infrared at 6.00μ was also reported earlier^{4,5} to be formed by heating the *O*-nitroso-compound alone or with oxygen at 100° , and hydrolysis of some *O*-nitroso-compound fractions recovered from photochemical experiments facilitated the isolation of the same compound, now identified as bistrifluoromethylnitramine.

Hydrolysis by 50% aqueous hydrochloric acid of a sample of *O*-nitrosobistrifluoromethylhydroxylamine, obtained by irradiation of trifluoronitrosomethane and known to be 95% pure, gave 94% of *NN*-bistrifluoromethylhydroxylamine,⁴ indicating that hydrolysis of the *O*-nitroso-compound was essentially quantitative. The unhydrolysed 5% impurity consisted mainly of bistrifluoromethylnitramine, identical with the compound synthesised from bistrifluoromethylamine:



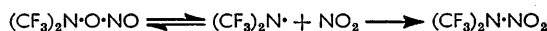
³ Banus, *J.*, 1953, 3755.

⁴ Jander and Haszeldine, *J.*, 1954, 912; Haszeldine and Mattinson, *J.*, 1957, 1741.

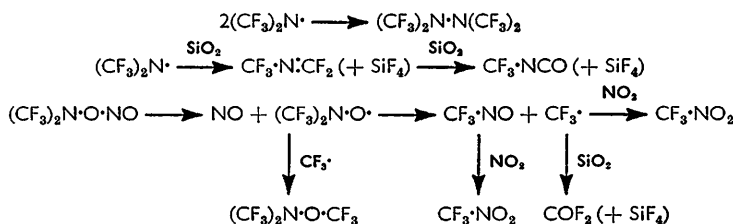
⁵ Haszeldine and Jander, *J.*, 1954, 696.

Bistrifluoromethylnitramine was also obtained when *O*-nitrosobistrifluoromethylhydroxylamine was heated at 80°; trifluoronitromethane, trifluoromethyl isocyanate, perfluoro(methylenemethylamine), perfluorotetramethylhydrazine and tristrifluoromethylhydroxylamine were also present, together with decomposition products such as nitrogen, carbon dioxide, carbonyl fluoride, and silicon tetrafluoride; the yield of the nitramine was not improved by heating the hydroxylamine in the presence of oxygen.

A free-radical mechanism is suggested for the thermal or photochemical rearrangement of the *O*-nitroso-compound into the *N*-nitro-compound:



Other products can arise as follows:



Bistrifluoromethylnitramine. The 60 Mc./sec. ^{19}F nuclear magnetic resonance (n.m.r.) spectrum of bistrifluoromethylnitramine is a singlet, with no fine structure, at 16.8 p.p.m. to low-field of trifluoroacetic acid as external reference. This indicates that all fluorine atoms are chemically equivalent and that any coupling to ^{14}N nuclei is either small or collapsed by rapid quadrupolar relaxation of these nuclei.

The 5.99 μ band in the infrared is assigned to the asymmetric NO_2 stretching vibration (cf. $\text{CF}_3\cdot\text{NO}_2$ 6.13, 6.17 μ),⁴ the 9.97 μ band to the C-N stretching vibration in the groups $(\text{CF}_3)_2\text{N}$, the 12.15 and 13.20 μ bands to the C-N-C bending vibrations, and the 13.75 μ band to CF_3 deformation.

The 275 $m\mu$ band (ϵ 37) in the ultraviolet spectrum of the nitramine vapour is ascribed to the NO_2 chromophore, with little or no conjugation from the lone pair on the $(\text{CF}_3)_2\text{N}$ groups, so that in this region the spectrum resembles that of trifluoronitromethane (λ_{max} 279; ϵ 11.0).⁴ A second band, at 237 $m\mu$ (ϵ 58), distinguishes the nitramine from a *C*-nitro-compound, and is in the same region as found for dimethylnitramine. Precise comparison with dimethylnitramine is difficult however, since the relatively high boiling point of this compound makes determination of its vapour spectrum difficult, and solvent effects are probably important in the reported high-intensity solution spectra (λ_{max} 240 $m\mu$, ϵ 6300, in dioxan; 238 $m\mu$, ϵ 8000, in water).⁶

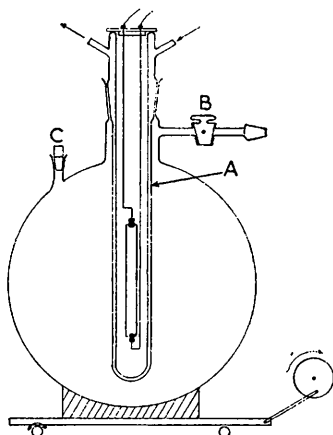
EXPERIMENTAL

A conventional vacuum system was used for the manipulation of volatile compounds, to prevent interference by air or moisture. Unless otherwise stated, reactions were carried out in sealed, evacuated tubes. Infrared spectra were recorded on a Perkin-Elmer 21 spectrometer with rock-salt optics, the ultraviolet spectra on a Unicam S.P. 500 instrument, and the n.m.r. spectra on an A.E.I. R.S.2 instrument.

Preparation and Purification of Trifluoronitrosomethane.—(a) *Recommended procedure.* The apparatus, shown in the Figure, consists of a double-walled (1 cm. gap) silica pocket A, reaching to 3 in. from the bottom of a 20 l. Pyrex flask, and fitted to it by a C70 joint sealed with Picein wax. A Hanovia S500 hot mercury lamp, generating mainly 2537 Å radiation, is supported in the lower portion of the silica pocket. Cooling water is circulated through the annular jacket and around the greased stopcock B and B14 joint C. To the dried, evacuated flask containing mercury (300 ml.), was added trifluoroiodomethane (73.3 g., 0.374 mole) followed by nitric oxide (11.3 g., 0.377 mole) through B. The pressure inside the flask was

⁶ Jones and Thom, *Canad. J. Res.*, 1949, **27**, B, 828; Kortion and Finckh, *Z. phys. chem.*, 1940, **48**, B, 32.

measured by a mercury manometer attached to C. The flask was then clamped on to a reciprocating shaker (75 strokes/min.) to keep the mercury surface agitated throughout the irradiation to facilitate rapid reaction with dinitrogen tetroxide generated during the reaction, and particularly during the removal of the excess of nitric oxide by air oxidation at the end of the reaction. The flask temperature rose to 15–20° above that of the room (20°) during irradiation; the initial pressure rise caused by this temperature increase was followed by a steady drop in pressure to half of the initial value in 3–4 hr. depending upon the age and efficiency of the ultraviolet lamp. Irradiation was stopped at this point, corresponding to the ideal conversion $2\text{CF}_3\text{I} + 2\text{NO} \rightarrow 2\text{CF}_3\text{NO} + \text{I}_2$, since over-irradiation increased the yield of the dimer $(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{NO}$ at the expense of trifluoronitrosomethane. Under-irradiation gave a high yield of the nitroso-compound (85%) but the conversion fell (30%).



Photochemical reactor

Air was then admitted through B, and shaking was continued for 1 hr. to remove dinitrogen tetroxide formed by oxidation of residual nitric oxide; this was the major function of the mercury. The flask was then slowly pumped out *via* three traps cooled in liquid nitrogen, and trifluoroiodomethane and *O*-nitrosobistrifluoromethylhydroxylamine were separated from the condensate by fractional condensation, *in vacuo*, then redistilled and separated at atmospheric pressure in an efficient low-temperature column with reflux head at -78° . The crude trifluoronitrosomethane was freed from acid gases by passing it rapidly through 30% aqueous sodium hydroxide, then finally purified by distillation through an efficient low-temperature column with reflux head cooled by liquid nitrogen. Its measured b. p., $-86.0^\circ/767$ mm., compares well with that calculated⁴ ($-86.6^\circ/760$ mm.) from vapour-pressure measurements. Infrared-spectroscopic analysis was used to check its purity. Traces of hexafluoroethane and nitrous oxide were the most difficult to remove, and for most reactions involving trifluoronitrosomethane they can be ignored.

Under optimum conditions (NO : CF_3I = 1 : 1; initial pressure 700–760 mm.; mercury present; excess of nitric oxide removed by air oxidation then reaction with mercury; temp. 35–50°; reaction time 3–4 hr. to 50% pressure drop; 500w mercury ultraviolet lamp) the products were trifluoronitrosomethane (21.2 g., 0.214 mole; 57% conversion, 80% yield), trifluoroiodomethane (20.6 g., 0.105 mole; 28% recovered), and *O*-nitrosobistrifluoromethylhydroxylamine (3.0 g., 0.015 mole; 8% conversion, 11% yield).

(b) *Effect of reaction variables.* A 500w ultraviolet lamp is preferred, since it shortens the irradiation time considerably compared with the 7w and 250w lamps described in earlier Papers.³

Table 1 shows some typical results, reproducible to $\pm 2\%$, taken from a large number of experiments designed to determine optimum conditions for the preparation of trifluoronitrosomethane. Decrease in initial pressure from 710 to 400 mm. gave a 6% increase in conversion, but an 8% decrease in yield, and the actual weight of trifluoronitrosomethane produced per experiment was considerably reduced. The conversion was higher (69%) if the NO : CF_3I ratio was increased from 1.2 : 1 to 1.4 : 1, but the yield was lower and wasteful on trifluoroiodomethane.

TABLE 1

Expt.	NO : CF ₃ I	Initial pressure (mm.)	Conversion CF ₃ I → CF ₃ NO (%)	Yield of CF ₃ NO on CF ₃ I consumed (%)	Wt. of CF ₃ NO (g.)	Fate of NO
1	1 : 1	710	57	80	21.2	Oxidised by air
2	1 : 1	400	63	72	14.0	" " "
3	1.2 : 1	640	59	75	17.7	" " "
4	1.4 : 1	690	69	70	20.8	" " "
5	1 : 1	690	48	(67) *	18.1	Pumped away
6	1 : 1	680	46	(70) *	17.1	Oxidised by air, no mercury present

* Impure.

That removal of the excess of nitric oxide by pumping on its mixture with trifluoronitrosomethane held at -160° causes a decrease in conversion and yield is clearly shown by experiment 5 in Table 1. The trifluoronitrosomethane so obtained was still impure and, when kept, soon decomposed further by reaction with the residual nitric oxide. Separate experiments showed that nitric oxide reacts rapidly with trifluoronitrosomethane in the liquid phase, and readily in the gas phase.

The advantage of having mercury present has been questioned, but experiment 6 shows that conversion and yield are reduced when mercury is absent during the reaction and also during the removal of nitric oxide at the end of reaction *via* its oxidation to dinitrogen tetroxide. Purification by distillation of trifluoronitrosomethane mixed with dinitrogen tetroxide is difficult and wasteful, and yields impure nitroso-compound. Trifluoronitromethane becomes a major by-product.

Irradiation of Trifluoronitrosomethane. The nitroso-compound (23.80 g., 0.241 mole) was irradiated in the 20 l. photochemical reactor, with results shown in Table 2. Nitrogen (50 ml.; *M*, 28) was measured as the only non-condensable product; dinitrogen tetroxide (340 ml.) was measured by the reduction in volume on shaking with mercury; carbon dioxide, carbonyl fluoride, and silicon tetrafluoride (480 ml.), detected by infrared spectroscopy, were removed by treatment with aqueous base (total 2.0 g.; 8%). Distillation and gas-liquid chromatographic examination gave trifluoronitrosomethane (8.12 g., 0.082 mole; 34%), *O*-nitrosobis-trifluoromethylhydroxylamine (12.55 g., 0.063 mole; 79% yield, 53% conversion) and trifluoronitromethane (0.36 g., 0.003 mole; 4% yield).

In another experiment, the same initial pressure was used in a 2.2 l. silica flask irradiated by a Hanovia S500 lamp placed 3 in. from it. The pressure after 29 hr. was 183 mm., and starting material (0.410 g., 4.2 mmoles, 16%), the hydroxylamine (1.518 g., 7.7 mmoles, 69% yield, 58% conversion), dinitrogen tetroxide (0.164 g., 3.57 mmoles; 32% yield), and carbon dioxide,

TABLE 2

Irradiation of trifluoronitrosomethane

Time (hr.)	0	0.083	0.167	0.25	0.50	0.75	1.0	2.0	3.0	4.0	5.0	7.0
Pressure (mm.)	227	229	227	223	216	213	210	199	196	193	192	191

carbonyl fluoride, and silicon tetrafluoride (0.407 g., 6.24 mmoles, 28% yield) were isolated.

Irradiation of O-Nitrosobis-trifluoromethylhydroxylamine.—This compound (26.05 g., 0.133 mole) was irradiated in the 20 l. reactor for 29 hr., with conditions similar to those yielding the results in Table 2. The change in pressure with time is shown in Table 3. The compounds isolated were starting material (22.18 g., 0.112 mole; 84%) trifluoronitrosomethane (0.838 g.,

TABLE 3

Irradiation of *O*-nitrosobis-trifluoromethylhydroxylamine

Time (hr.)	0	0.25	1.25	4.0	7.0	19.0	22.0	23.5	26.5	29.0
Pressure (mm.)	127	135	139	144	150	164	167	169	170	170

8.5 mmoles; 20% yield, 3% conversion), trifluoronitromethane (0.51 g., 4 mmoles; 10% yield, 2% conversion), dinitrogen tetroxide (0.41 g., 9 mmoles; 43% yield, 2% conversion), and carbonyl fluoride, silicon tetrafluoride, and carbon dioxide (1.47 g., 22 mmoles; 52% yield). The respective yields after a 7 hr. reaction were starting material (16.7 g., 84.7 mmoles, 84%

recovered), trifluoronitrosomethane (0.795 g., 8.0 mmoles, 25% yield, 4% conversion), trifluoronitromethane (0.51 g., 4.0 mmoles, 12% yield, 2% conversion) and decomposition products (0.51 g., 9.0 mmoles, 25% yield).

It thus appears that the apparent equilibrium is attained more rapidly on irradiation of the dimer, but allowance must be made for the fact that the ultraviolet and visible bands emitted by the ultraviolet lamps can be absorbed more readily by the dimer than by the monomer. Furthermore, since the CF_3NO : dimer ratio was 1 : 10.6 after 7 hr. and 1 : 13 after 29 hr., some of the trifluoronitrosomethane formed initially was being destroyed by other reactions of the type discussed, so that a true equilibrium cannot be attained. The CF_3NO : dimer ratio after 7 hr. irradiation of trifluoronitrosomethane was 1 : 3.

Bistrifluoromethylnitramine. (a) *From irradiation of trifluoronitrosomethane or O-nitrosobistrifluoromethylhydroxylamine.* A specimen of *O*-nitrosobistrifluoromethylhydroxylamine (1.845 g., 9.29 mmoles) (Found: *M*, 199; purity by gas-liquid chromatography 95%) obtained by photochemical dimerisation of trifluoronitrosomethane followed by distillation, was sealed *in vacuo* in a 120 ml. Pyrex tube with mercury (1.5 ml.) and 50% (v/v) aqueous hydrochloric acid (3 ml.), and shaken at room temperature until colourless (15–24 hr.).⁴ Distillation gave *NN*-bistrifluoromethylhydroxylamine (1.478 g., 8.74 mmoles; 94% conversion) (Found: *M*, 169. Calc. for $\text{C}_2\text{HF}_6\text{NO}$: *M*, 169) identified by means of its infrared spectrum, together with a four-component mixture (0.059 g., 0.27 mmole; 3% conversion) (Found: *M*, 218). Approximately 50% of this last mixture was bistrifluoromethylnitramine (Found: C, 12.0; N, 14.2%; *M*, 197. Calc. for $\text{C}_2\text{F}_6\text{N}_2\text{O}_2$: C, 12.1; N, 14.1%; *M*, 198), isolated by gas-liquid chromatography (4 m. 30% dinonyl phthalate-Celite column at 20°) of the combined fractions from several experiments on this scale; tristrifluoromethylhydroxylamine and perfluorotetramethylhydrazine were also identified in the mixture.

Investigation of the *O*-nitrosobistrifluoromethylhydroxylamine fraction recovered from prolonged irradiation of the *O*-nitroso-compound gave similar results.

The vapour pressure of bistrifluoromethylnitramine over the range -28° to 12° is given by the equation $\log_{10} p(\text{mm.}) = 7.716 - 1399/T$, whence the b. p. is calculated as 16.4° , the latent heat of vaporisation as $6410 \text{ cal. mole}^{-1}$, and Trouton's constant as 22.3 .

(b) *From bistrifluoromethylamine.* A solution of 70% nitric acid (1 ml., 15 mmoles) in trifluoroacetic anhydride (9.9 g., 6 ml., 47 mmoles) in a 40 ml. tube was cooled in liquid nitrogen and the tube evacuated. Bistrifluoromethylamine⁵ (0.694 g., 4.66 mmoles) was condensed in, the tube sealed, and allowed to warm to room temperature during 2.5 hr. The straw-coloured liquid turned brown when heated at 50° (1 hr.). Dinitrogen tetroxide in the volatile products was removed by shaking with mercury, and distillation of the residual gas gave a mixture of bistrifluoromethylamine (17%) and bistrifluoromethylnitramine containing traces of trifluoromethyl isocyanate and trifluoroacetic anhydride. The mixture was washed with 5% aqueous sodium hydroxide for 5 min. to give pure bistrifluoromethylnitramine (0.720 g., 3.62 mmoles; 93% yield, 78% conversion) (Found: *M*, 198), with the same physical properties as the material isolated in (a).

The above sealed-tube method for the preparation of the nitramine gives a very much improved yield over that reported in the literature (43%);⁷ the material then obtained had b. p. 17° , but decomposed slowly when kept. Pure bistrifluoromethylnitramine can be stored without decomposition in Pyrex ampoules in the absence of air.

(c) *By pyrolysis of O-nitrosobistrifluoromethylhydroxylamine.* The nitroso-compound (1.88 g., 9.49 mmole), heated at 78° in a 48 ml. Pyrex tube for 14 days gave nitrogen (0.052 g., 1.87 mmoles; 20% yield), carbon dioxide, carbonyl fluoride, and silicon tetrafluoride (0.580 g., 7.57 mmole), recovered *O*-nitrosobistrifluoromethylhydroxylamine (0.90 g., 4.55 mmoles; 48% yield), trifluoronitromethane (0.13 g., 1.14 mmoles; 12% yield), trifluoromethyl isocyanate (0.094 g., 0.85 mmoles; 17% yield), perfluoro(methylenemethylamine) (0.040 g., 0.30 mmoles; 6% yield), and bistrifluoromethylnitramine (0.057 g., 0.29 mmoles; 6% yield). Perfluoro-tetramethylhydrazine and tristrifluoromethylhydroxylamine⁸ were also detected. Product analysis involved fractionation *in vacuo*, and a combination of infrared-spectroscopic and gas-liquid chromatographic analysis, together with molecular-weight determinations.

(d) *By pyrolysis of O-nitrosobistrifluoromethylhydroxylamine in presence of oxygen.* Reaction (c), repeated with the addition of oxygen in a 2 : 1 ratio, gave starting material (0.425 g.,

⁷ Young, Tsoukalas, and Dresdner, *J. Amer. Chem. Soc.*, 1958, **80**, 3604.

⁸ Described in Part XIII, following Paper.

2.15 mmoles, 50%), trifluoronitromethane (0.144 g., 1.25 mmoles, 29% yield), trifluoromethyl isocyanate (0.071 g., 0.64 mmoles, 30% yield), bistrifluoromethylnitramine (0.016 g., 0.08 mmoles, 4% yield), perfluoro(methylenemethylamine) (0.011 g., 0.08 mmoles, 4% yield), and dinitrogen tetroxide (0.019 g., 0.21 mmoles, 10% yield).

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