329. *Perfluoroalkyl Derivatives of Nitrogen. Part VI.** NN-*Bistrifluoromethylhydroxylamine, the Structure of Trifluoronitrosomethane Dimer, and the Direction of Free-radical Addition to a Nitroso-group.*†

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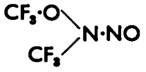
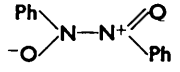
Trifluoronitrosomethane dimer, produced photochemically from trifluoronitrosomethane, is shown by chemical and spectroscopic studies to be $(CF_3)_2N{\cdot}O{\cdot}NO$. Attack of a free CF_3 radical is thus on the nitrogen atom of the N:O group, and not on the oxygen as was tentatively concluded earlier. Reaction of *O*-nitrosobistrifluoromethylhydroxylamine (bistrifluoromethylhydroxylamine nitrite) with methanol or aqueous hydrogen chloride yields *NN*-bistrifluoromethylhydroxylamine. Phosphorus pentachloride converts the last compound into *N*-chlorobistrifluoromethylamine, which oxidises hydrogen chloride to chlorine and is itself reduced to bistrifluoromethylamine.

Trifluoronitrosomethane,[1] a deep-blue gas, yields an orange-red dimer [2] quantitatively when exposed to light. It was concluded [2] that the dimer was (I) or (II), and not a dimer analogous to that (III) of nitrosobenzene. Although initial infrared-spectroscopic studies [3] suggested that (I) was more probable than (II), further studies on the spectra of nitrosamines and nitrites,[4] and the synthesis of suitable reference compounds,[1] together with chemical evidence, now show that this was incorrect: *O*-nitrosobistrifluoromethylhydroxylamine (II) is the correct structure for the dimer of trifluoronitrosomethane.


(I)

$(CF_3)_2N{\cdot}O{\cdot}NO$

(II)


(III) (*cis or trans*)

Chemical Evidence.—Two procedures have proved successful for the conversion of the nitrite (II) into the parent hydroxylamine $(CF_3)_2N{\cdot}OH$. The strongly electronegative CF_3 groups make possible the equilibrium:

$$\underset{\text{B. p. } 10^\circ}{(CF_3)_2N{\cdot}O{\cdot}NO} + CH_3{\cdot}OH \rightleftharpoons \underset{\substack{\text{B. p. } 35^\circ \\ \text{(predicted)}}}{(CF_3)_2N{\cdot}OH} + \underset{\text{B. p. } -12^\circ}{CH_3{\cdot}O{\cdot}NO}$$

and the volatility of methyl nitrite enables it to be removed by distillation as formed, so displacing the equilibrium; *NN*-bistrifluoromethylhydroxylamine was thus isolated (75% yield; b. p. 32·5°).

The reaction:

$$(CF_3)_2N{\cdot}O{\cdot}NO + HCl\ (aq.) \rightleftharpoons (CF_3)_2N{\cdot}OH + NOCl$$

is probably also an equilibrium, and removal of nitrosyl chloride by reaction with mercury enables *NN*-bistrifluoromethylhydroxylamine to be prepared more conveniently (72% yield) than by the first method.

The boiling point of bistrifluoromethylhydroxylamine (32·5°) suggests, by comparison with that of the amine $(CF_3)_2NH$ (−6·7°),[1] that hydrogen bonding is not very pronounced, despite the fact that the hydrogen will be more acidic than in, say, *NN*-dimethylhydroxylamine; the reduced basicity of the nitrogen and the oxygen is clearly more important,

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* Part V, *J.*, 1957, 30.

† For a preliminary communication see *Chem. and Ind.*, 1956, 81.

[1] Barr and Haszeldine, *J.*, 1955, 1881, 2532, where earlier references are given.

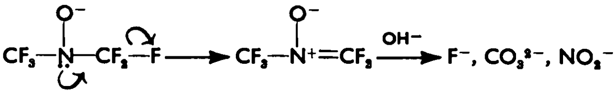
[2] Haszeldine and Jander, *J.*, 1954, 696.

[3] *Idem*, *J.*, 1954, 691.

[4] Haszeldine and Mattinson, *J.*, 1955, 4172.

and the situation resembles that in polyfluoro-alcohols.[5] The boiling point of *NN*-dimethylhydroxylamine[6] is 95°. *NN*-Bistrifluoromethylhydroxylamine is stable to an aqueous solution containing 5% (v/v) of concentrated hydrochloric acid, but is decomposed slowly by 2% aqueous sodium hydroxide to give fluoride and nitrite, possibly *via* initial elimination of fluoride:[1]

$$(CF_3)_2N{\cdot}OH \xrightarrow{NaOH} (CF_3)_2N{\cdot}O^-$$



$$CF_3{-}\overset{O^-}{\overset{|}{N}}{-}CF_2{-}F \longrightarrow CF_3{-}\overset{O^-}{\overset{|}{N^+}}{=}CF_2 \xrightarrow{OH^-} F^-,\ CO_3^{2-},\ NO_2^-$$

The structure of *NN*-bistrifluoromethylhydroxylamine was proved by its reaction with phosphorus pentachloride to give the known[1] bistrifluoromethylamine in 80% yield. This eliminates the possibility that the compound of b. p. 32·5° was actually the compound $(CF_3)(CF_3{\cdot}O)NH$ arising by the reactions

$$(CF_3)(CF_3{\cdot}O)N{\cdot}NO + CH_3{\cdot}OH \rightleftharpoons (CF_3)(CF_3{\cdot}O)NH + CH_3{\cdot}O{\cdot}NO$$

$$(CF_3)(CF_3{\cdot}O)N{\cdot}NO + HCl \rightleftharpoons (CF_3)(CF_3{\cdot}O)NH + NOCl$$

since reaction with phosphorus pentachloride could clearly not convert this compound into bistrifluoromethylamine. The stability of the compound, b. p. 32·5°, to water and aqueous acid also proves that the compound $(CF_3)(CF_3{\cdot}O)NH$ is not present, since it is known[1] that compounds containing the $-CF_2{\cdot}NH-$ group are stable only in solvents of low dielectric constant and decompose in water by initial loss of hydrogen fluoride; by analogy with bistrifluoromethylamine, decomposition would occur as follows:

$$CF_3{\cdot}O{\cdot}NH{\cdot}CF_3 \xrightarrow{-HF} CF_3{\cdot}O{\cdot}N{:}CF_2 \xrightarrow{H_2O} CF_3{\cdot}O{\cdot}N{:}C{:}O$$

$$CF_3{\cdot}O{\cdot}N{:}C{:}O \xrightarrow{H_2O} CF_3{\cdot}O{\cdot}NH_2 \longrightarrow CF_3{\cdot}OH, NH_2{\cdot}OH, F^-, CO_3^{2-}$$

The formation of bistrifluoromethylamine by reaction of *NN*-bistrifluoromethylhydroxylamine with phosphorus pentachloride clearly involves the intermediate formation of *N*-chlorobistrifluoromethylamine; the two CF_3 groups make the chlorine atom in this compound extremely "positive," and the oxidation of hydrogen chloride explains the formation of free chlorine at 50°:

$$(CF_3)_2N{\cdot}OH + PCl_5 \longrightarrow (CF_3)_2NCl + POCl_3 + HCl$$

$$(CF_3)_2\overset{\delta-}{N}{-}\overset{\delta+}{Cl} + HCl \longrightarrow (CF_3)_2NH + Cl_2$$

Reaction of *NN*-bistrifluoromethylhydroxylamine with phosphorus pentachloride at room temperature liberates the theoretical amount of hydrogen chloride within a few minutes, and free chlorine begins to appear only after 1—2 hours or when the reactants are heated. The presence in the early stages of the room-temperature reaction of the reactive compound $(CF_3)_2NCl$ is apparent from qualitative tests and spectroscopic examination, but an attempt to separate it from the phosphorus oxychloride failed on the scale used, despite the predicted appreciable difference in boiling point. Reaction with mercury converts the *N*-chloro-compound into a compound of much higher molecular weight, doubtless tetrakistrifluoromethylhydrazine:

$$2(CF_3)_2NCl + Hg \longrightarrow (CF_3)_2N{\cdot}N(CF_3)_2 + HgCl_2$$

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[5] Haszeldine, *J.*, 1953, 1757.

[6] Hepworth, *J.*, 1921, 251.

Bistrifluoromethylamine fails to react photochemically with chlorine, thus showing, not unexpectedly, that the equilibria:

$$(CF_3)_2NH \underset{HCl}{\overset{Cl\cdot}{\rightleftharpoons}} (CF_3)_2N\cdot \underset{h\nu}{\overset{Cl_2}{\rightleftharpoons}} (CF_3)_2NCl$$

lie to the left.

Spectroscopic Evidence.—Fluorine-free nitrosamines and nitrites can be distinguished by the marked shift to the blue which occurs for the nitrosamine spectrum as the solvent becomes more polar,[4] but clear-cut distinction cannot be made from vapour spectra alone. Fluorine in the β-position of a nitrosamine or nitrite causes a shift to the red of 6—10 mμ for the main ultraviolet maxima for the vapour,[4] but again distinction between the two cannot be made. However, the equilibrium:

$$R\cdot CH_2\cdot O\cdot NO + C_2H_5\cdot OH \rightleftharpoons R\cdot CH_2\cdot OH + C_2H_5O\cdot NO$$

lies well to the right when R = fluoroalkyl and the ultraviolet spectrum of a fluoroalkyl nitrite in ethanol is thus essentially that of ethanolic ethyl nitrite and quite different from the spectrum of the fluoroalkyl nitrite as a vapour or as a solution in light petroleum. By contrast, the ultraviolet spectrum of a fluoroalkylnitrosamine is scarcely altered by change from vapour to solution in ethanol and is quite distinct from that of ethyl nitrite.[4] Distinction between a nitrosamine and a nitrite each containing fluorine near to the N·NO or O·NO system can thus be made by observing if the spectrum remains virtually unchanged in ethanolic solution (fluoro-nitrosamine) or changes to that of ethyl nitrite (fluoro-nitrite).

The presence of the nitrite structure in trifluoronitrosomethane dimer is strongly suggested by the fact that the spectrum of its solution in light petroleum is essentially the same as that of the vapour (Table), whereas the spectrum of its ethanolic solution is identical with that of ethanolic ethyl nitrite [386 (infl.), 370, 357 (main peak), 345, 334, 324, and 314 mμ]. The shift to the red of the main nitrite peak observed for trifluoroethyl nitrite[4] is thus continued with *O*-nitrosobistrifluoromethylhydroxylamine: EtO·NO 355; $CF_3\cdot CH_2\cdot O\cdot NO$ 364; $(CF_3)_2N\cdot O\cdot NO$ 374 mμ.

Ultraviolet spectra (300—450 mμ).*

	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε		$\lambda_{max.}$	$\lambda_{min.}$
$(CF_3)_2N\cdot O\cdot NO$	448	6·6	447	6·5	$CF_3\cdot CH_2\cdot O\cdot NO$	381	374
vapour	445	6·9	444	6·8	in light	364	358
	439	7·6	438	7·5	petroleum	351	344
	380	16·30	379	16·10		337	330
	374·5	16·70	374	16·60		325	320
	372	16·69	371	16·50		314 *	—
	368	16·60	367	16·40			
	366	16·60	322·5	8·6			
	317·5	9·64	316	9·3			

* See ref. 4 for vapour and solution spectra of $CF_3\cdot CH_2\cdot O\cdot NO$ and $(CF_3\cdot CH_2)_2N\cdot NO$.

Our further studies[4] on the infrared spectra of dialkylnitrosamines have shown that strong dipolar interaction occurs in the liquid or in solution with consequent marked shift of the N:O vibration [*e.g.*, $Me_2N\cdot NO$: vapour 6·72 μ (monomer); CCl_4 solution 6·88 μ (monomer), 7·63 μ ("dimer"); liquid 6·92 μ (monomer), 7·60 μ: ("dimer")]. The original infrared spectroscopic evidence[3] for the structure of trifluoronitrosomethane dimer is thus invalidated, and it is now clear that the N:O vibration for (I) would lie between 5·9 and 6·4 μ [cf. $Me_2N\cdot NO$ 6·72 μ; $(CF_3\cdot CH_2)_2N\cdot NO$ 6·45 μ], where the trifluoronitrosomethane dimer actually shows only weak absorption. By contrast, extrapolation of the N:O vibration for EtO·NO (5·97 μ) and $CF_3\cdot CH_2\cdot O\cdot NO$ (5·76 μ) to $(CF_3)_2N\cdot O\cdot NO$ gives a predicted value for the N:O vibration of 5·4—5·7 μ, and the distinct doublet at

5·47, 5·55 μ in the spectrum of trifluoronitrosomethane dimer is now to be assigned to the N⁚O vibration in *O*-nitrosobistrifluoromethylhydroxylamine.

Free-radical Addition to a Nitroso-group.—The elucidation of the structure of trifluoronitrosomethane dimer as *O*-nitrosobistrifluoromethylhydroxylamine establishes the direction of free-radical addition to a nitroso-group:

$$\begin{aligned} & CF_3{\cdot}NO \xrightarrow{h\nu} CF_3{\cdot} + NO \\ & CF_3{\cdot} + CF_3{\cdot}N{:}O \longrightarrow (CF_3)_2N{\cdot}O{\cdot} \\ & (CF_3)_2N{\cdot}O{\cdot} + NO \longrightarrow (CF_3)_2N{\cdot}O{\cdot}NO \\ \text{or} \quad & (CF_3)_2N{\cdot}O{\cdot} + CF_3{\cdot}NO \longrightarrow (CF_3)_2N{\cdot}O{\cdot}NO + CF_3{\cdot} \longrightarrow \text{etc.} \end{aligned}$$

The CF_3 radical clearly attacks nitrogen in preference to oxygen. The nitroso-group in trifluoronitrosomethane, prevented from forming a dimer of the nitrosobenzene type (III), thus reacts in many ways like a C⁚C double bond, undergoing nucleophilic [1] or free-radical attack, and is capable o fgiving a · · · N·O·C·C · · · copolymer or an oxazetidine $-\overline{N-O-C-C}-$ with olefins.[1, 7]

EXPERIMENTAL

Preparation of O-*Nitrosobistrifluoromethylhydroxylamine* [NN-*Bistrifluoromethylhydroxylamine Nitrite*].—In a typical experiment, trifluoronitrosomethane (0·0566 mole) in a sealed 188-ml. silica tube was exposed to ultraviolet and visible radiation from a Hanovia arc for 40 hr. The lower 2″ of the tube were covered by black paper to shield liquid products from further irradiation. A small amount (*ca.* 0·0001 mole) of a non-condensable gas was discarded, and the reaction products were distilled *in vacuo*, to give unchanged trifluoronitrosomethane (0·0105 mole, 18%), carbon dioxide (0·0016 mole, 4%; separated from the trifluoronitrosomethane by treatment with aqueous sodium hydroxide), and O-*nitrosobistrifluoromethylhydroxylamine* (0·0221 mole, 96% based on $CF_3{\cdot}NO$ used) (Found: C, 12·0; N, 14·2%; *M*, 198. $C_2O_2N_2F_6$ requires C, 12·1; N, 14·1%; *M*, 198), b. p. 10°, as a red-brown liquid changing to a yellow solid when cooled. Over-irradiation caused some formation of dinitrogen tetroxide, but this may be removed by shaking the crude product with mercury before fractionation.

Bistrifluoromethylhydroxylamine.—Method A. Methanol (2·29 ml., 10% excess; dried by CaO under reflux, followed by Mg under reflux, then fractionated) was frozen in a 20-ml. flask fitted with a vertical condenser cooled over a 25 cm. length by ice–salt at −10°, leading to traps cooled by liquid oxygen. The apparatus was evacuated and *O*-nitrosobistrifluoromethylhydroxylamine (10·3 g., 0·0519 mole) was condensed into the flask; dry nitrogen was then admitted until the pressure reached atmospheric. The reactants were warmed to 0°, whereupon methyl nitrite (b. p. −12°) slowly began to condense in the traps. The reactants were gradually heated from 0° to 40° during 7 hr., and during the last hour unchanged *O*-nitrosobistrifluoromethylhydroxylamine was under reflux. The contents of the traps and the flask were fractionated separately, to give unchanged *O*-nitrosobistrifluoromethylhydroxylamine (0·0144 mole, 28%), methyl nitrite (0·0320 mole, 85%), *bistrifluoromethylhydroxylamine* (3·92 g., 62%), b. p. 32·5° (isoteniscope) (Found: C, 14·0; H, 0·7; N, 8·3%; *M*, 169. C_2HONF_6 requires C, 14·2; H, 0·6; N, 8·3%; *M*, 169), and a mixture of bistrifluoromethylhydroxylamine (0·005 mole) and methanol. The total yield of the bistrifluoromethylhydroxylamine based on the *O*-nitroso-compound used (72%) is thus 75%. It was not possible to separate methanol and bistrifluoromethylhydroxylamine by distillation on the scale used, and azeotrope formation is probable; final removal of methanol was effected by treatment thrice with an excess of "AnalaR" calcium chloride.

Method B. Mercury (1 ml.), aqueous hydrochloric acid (1·34 ml., containing 50% (v/v) of conc. acid 100% excess), and *O*-nitrosobistrifluoromethylhydroxylamine (0·774 g., 0·00391 mole) in a sealed Pyrex tube were allowed to warm from liquid-oxygen temperature to that of the room. Rapid reaction was apparent, the mercury was soon attacked, and the red-brown colour typical of the *O*-nitroso-compound faded to a pale yellow. The tube was then shaken

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[7] Barr and Haszeldine, *Nature*, 1955, **175**, 991.

for 16 hr. without apparent change in colour. Fractionation gave bistrifluoromethylhydroxylamine (0·00280 mole, 72%) (Found: *M*, 169. Calc. for C_2HONF_6: *M*, 169), shown to be identical with the compound prepared by Method *A* by comparison of infrared spectra. A pale green liquid (0·0077 mole, equiv. to 20% of starting material) (Found: *M*, 202) and small amounts of hydrogen chloride, carbon dioxide, and nitric oxide were also isolated.

Reactions of Bistrifluoromethylhydroxylamine.—(a) *Stability to acid.* The hydroxylamine (0·406 g.) and aqueous hydrogen chloride (0·82 ml., concn. as above) formed two sharply defined layers when sealed *in vacuo* in a 5-ml. Pyrex tube. The tube was shaken vigorously (16 hr.) and the more volatile products were then fractionated *in vacuo*, to give unchanged bistrifluoromethylhydroxylamine (0·404 g., 99·5%) (Found: *M*, 169), whose identity was confirmed by infrared spectroscopy.

(b) *Stability to aqueous alkali.* Bistrifluoromethylhydroxylamine (0·345 g., 0·00204 mole) was shaken with 2% aqueous potassium hydroxide (8·4 ml.) in a sealed 25-ml. Pyrex tube for 20 hr. at 20°. The unchanged bistrifluoromethylhydroxylamine (39%) was removed by fractionation *in vacuo*, and the acidified (dilute sulphuric acid) aqueous solution gave positive tests for fluoride (cerous nitrate) and nitrite.

(c) *With phosphorus pentachloride.* Finely powdered phosphorus pentachloride (5·5 g., 350% excess) was placed in a 35-ml. Pyrex tube which was then pumped out (1 hr.) before bistrifluoromethylhydroxylamine (1·0 g., 0·00591 mole) was condensed in and the tube sealed. After 1·5 hr. at 20° only a faint yellow colour was apparent and after 3 hr. the tube was heated to 50° for 21 hr., then set aside at 20° for 20 hr. The intensity of the yellow colour had then increased appreciably. Fractionation in a vacuum-apparatus free from mercury showed chlorine to be a product. The residual chlorine was removed from the main volatile products by reaction with mercury, and refractionation gave bistrifluoromethylamine (0·00474 mole, 80%) (Found: N, 9·0%; *M*, 153. Calc. for C_2HNF_6: N, 9·2%; *M*, 153) spectroscopically identical with a known sample,[3] hydrogen chloride (Found: *M*, 38·5. Calc. for HCl: *M*, 36·5), and phosphorus oxychloride (0·81 g., 89%), identified by means of its infrared spectrum.

In a second experiment bistrifluoromethylhydroxylamine (0·82 g., 0·0049 mole), shaken with phosphorus pentachloride (5·5 g.) at 20° for 40 min., gave hydrogen chloride (99·5%) (Found: *M*, 37·0), phosphorus oxychloride, and a compound which is probably *N*-chlorobistrifluoromethylamine, but no chlorine. *N*-Chlorobistrifluoromethylamine is difficult to separate from phosphorus oxychloride on the scale used; it reacts rapidly with mercury to give mercuric chloride and a liquid of vapour pressure approx. 95 mm. at 20° and molecular weight *ca.* 300 believed to be tetrakistrifluoromethylhydrazine (*M*, 304).

Reaction of Bistrifluoromethylamine with Chlorine.—The amine (2·08 g., 0·0136 mole; prepared as described earlier) and chlorine (0·704 g., 0·0099 mole) were exposed to ultraviolet light in a 190-ml. silica tube for 71 hr. Removal of the chlorine by reaction with mercury and fractionation *in vacuo* gave only unchanged bistrifluoromethylamine (99%) (Found: *M*, 154. Calc. for C_2HNF_6: *M*, 153), and in particular there was no indication of the formation of tetrakistrifluoromethylhydrazine.

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