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EXCHANGE REACTIONS BETWEEN O-NITROSOBIS(TRIFLUOROMETHYL)HYDROXYLAMINE AND $M(CF_3)_3$ (M = P, As and Sb)

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SUMMARY

O-Nitrosobis(trifluoromethyl)hydroxylamine gives novel reactions with tris(trifluoromethyl)-phosphine, -arsine and -stibine to afford mainly the corresponding bis(trifluoromethyl)nitroxyl derivatives. Tris(trifluoromethyl)phosphine affords $(CF_3)_2NOP(O)(CF_3)_2$ and $(CF_3)_2NNO$. Tris(trifluoromethyl)arsine also gives $(CF_3)_2NNO$ in high yield, together with smaller amounts of $(CF_3)_2NOAs(CF_3)_2$, $CF_3N = CF_2$, COF_2 and a polymeric white solid. With tris(trifluoromethyl)stibine, no oxidation nor addition reactions occurred. Instead, $[(CF_3)_2NO]_3Sb$ and $[(CF_3)NO]_2SbCF_3$ were obtained in high yields. The stoichiometry of the reactions suggests that the additional amounts of bis(trifluoromethyl)nitroxyl groups bonded to antimony are derived from the trifluoromethyl groups bonded to antimony. Mechanisms to rationalise these reactions are proposed.

INTRODUCTION

O-Nitrosobis(trifluoromethyl)hydroxylamine, $(CF_3)_2NONO$, first reported by Haszeldine and Jander in 1954 can be synthesized by several methods. It can be readily formed by the dimerisation of trifluoronitrosomethane[1, 2] or the reaction of bis(trifluoromethyl)nitroxyl with nitric oxide [3, 4].

Only a few reactions of O-nitrosobis(trifluoromethyl)hydroxylamine have been reported. Hydrolysis of O-nitrosobis(trifluoromethyl)-hydroxylamine with aqueous hydrochloric acid or 10% aqueous sodium hydroxide or methanol gives an almost quantitative yield of N,N-bis(trifluoromethyl)-hydroxylamine [1, 5]. Cleavage of the $(CF_3)_2NO$-NO bond occurs with PCl_5 and S_2F_{10} to afford $(CF_3)_2NOPCl$ and $(CF_3)_2NOSF_5$ respectively [6]. Pyrolysis, on the other hand, gives a mixture of products, namely $(CF_3)_2NNO_2$, $(CF_3)_2NOCF_3$, CF_3NCO, CF_3NO_2 and $(CF_3)_2NN(CF_3)_2$ [2, 7]. The mechanisms can be rationalised in terms of free radicals generated by the cleavage of $(CF_3)_2N$-ONO and $(CF_3)_2NO$-NO bonds. Our present studies highlight the ease of cleavage of the $(CF_3)_2NO$-NO bond in the reactions between O-nitrosobis-(trifluoromethyl)hydroxylamine and tris(trifluoromethyl)phosphine, arsine and stibine to give oxidation and substitution products. Mechanisms to explain some of the novel reactions are proposed.

RESULTS AND DISCUSSION

Reactions with tris(trifluoromethyl)phosphine

Tris(trifluoromethyl)phosphine does not react with O-nitrosobis-(trifluoromethyl)hydroxylamine at room temperature. When an equimolar mixture of the reactants was heated at 65°C for 30 hours, the reaction proceeded slowly as indicated by the disappearance of the orange-red colour of O-nitrosobis(trifluoromethyl)hydroxylamine. On further heating to 85°C for 24 hours, the colour of the mixture turned greenish-yellow.

On fractionation of the products, about 75% of the tris(trifluoromethyl)phosphine was recovered. All the O-nitrosobis(trifluoromethyl)-hydroxylamine had reacted.

The greenish-yellow gas that was trapped at the -120° trap (passed -96°C trap) was identified by its infrared spectrum [8], elemental analyses and molecular weight to be N-nitrosobis(trifluoromethyl)amine, $(CF_3)_2NNO$ (yield 80%).

The second fraction was a phosphorus compound isolated from -78°C trap. The infrared spectrum showed the typical absorptions of trifluoromethyl and bis(trifluoromethyl)nitroxyl groups bonded to the phosphorus atom (Table 1). The compound was identified as bis(trifluoromethyl)nitroxybis(trifluoromethyl)phosphine oxide (I), $(CF_3)_2NOP(O)(CF_3)_2$ (yield 54%).

Compound (I) was independently prepared in high yield by the reaction of bis(trifluoromethyl)phosphinic chloride, and mercury di-[bis(trifluoromethyl)nitroxide], according to the equation:

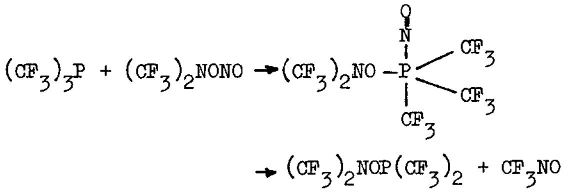
$$2(CF_3)_2P(O)Cl + [(CF_3)_2NO]_2Hg \rightarrow 2(CF_3)_2NOP(O)(CF_3)_2 + HgCl_2$$

Alkaline hydrolysis of compound (I) by 20% aqueous sodium hydroxide did not cleave the two trifluoromethyl groups from the phosphorus atom completely. The yield of trifluoromethane was 50%.

The colourless compound (I) is not attacked by chlorine. It is hydrolysed in air to give a heavy, non-volatile liquid.

The last fraction from the reactions between O-nitrosobis(trifluoromethyl)hydroxylamine with tris(trifluoromethyl)phosphine consists of a volatile mixture trapped at the -196° trap (passed -120°C trap). Only carbonyl fluoride and trifluoronitrosomethane were identified.

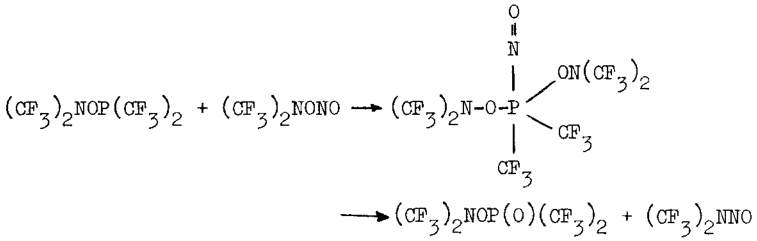
The formation of $(CF_3)_2NOP(O)(CF_3)_2$ and CF_3NO from the reactions between O-nitrosobis(trifluoromethyl)hydroxylamine and tris(trifluoromethyl)phosphine could have presumably been derived by oxidative addition followed by elimination reactions as shown by the following equations:



$$(CF_3)_3P + (CF_3)_2NONO \rightarrow (CF_3)_2NO-\overset{\overset{O}{\|}{N}}{\underset{CF_3}{P}}(CF_3)_2 \rightarrow (CF_3)_2NOP(CF_3)_2 + CF_3NO$$

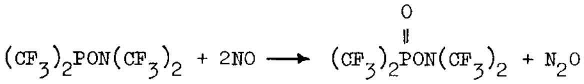
The process of oxidative addition followed by reductive elimination of substituted phosphines involving the NO-N bond has been reported previously by Ang and Lien [9].

The oxidation reaction can be rationalised according to the following equations:



Alternatively free radical mechanisms initiated by the cleavage of $(CF_3)_2NO$-NO bond are also possible.

The oxidation reaction of $(CF_3)_2PON(CF_3)_2$ can also proceed according to the equation:



$$(CF_3)_2PON(CF_3)_2 + 2NO \longrightarrow (CF_3)_2\overset{\overset{O}{\|}}{P}ON(CF_3)_2 + N_2O$$

because Dobbie has shown that oxidation of a number of substituted phosphines with nitric oxide give the corresponding oxides [10].

Reactions with tris(trifluoromethyl)arsine

An equimolar mixture of O-nitrosobis(trifluoromethyl)hydroxylamine and tris(trifluoromethyl)arsine was heated to 80°C for one day in a glass ampoule. The mixture gave a yellowish-green vapour and liquid together with some white solids. The O-nitrosobisfluoromethyl)hydroxylamine reacted completely; and 60% of the tris(trifluoromethyl)arsine was recovered.

The reaction gave predominantly N-nitrosobis(trifluoromethyl)amine, $(CF_3)_2NNO$ in 97% yield, based on the amount of O-nitrosobis(trifluoromethyl)hydroxylamine used.

A small amount of product (II) was trapped at -78°C (passed the -65°C trap) as a white solid liquid.

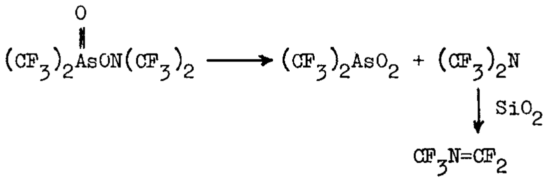
Its infrared spectrum showed the characteristic absorptions of $(CF_3)_2NO$ and $(CF_3)_2As$ groups, and similar to that of an authentic sample of bis(trifluoromethyl)nitroxybis(trifluoromethyl)arsine [11, 12].

Its reactions with hydrogen chloride gave N,N-bis(trifluoromethyl) hydroxylamine and chlorobis(trifluoromethyl)arsine. With 20% aqueous sodium hydroxide, product (II) afforded trifluoromethane as the only volatile product.

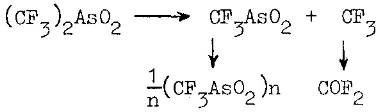
The most volatile fraction from the reactions of O-nitrosobis(trifluoromethyl)hydroxylamine with tris(trifluoromethyl)arsine was found at the -196°C trap (passed the -126° trap). It consisted mainly of carbonyl fluoride and perfluoro-2-azapropene.

After the removal of the volatile products, the substance left in the ampoule was a hygroscopic white solid, which gave off white fumes when exposed to air. The white solids, liberating trifluoromethane in 20% aqueous sodium hydroxide, could presumably be the polymeric arsenic compound, $(CF_3AsO_2)_n$.

Formation of the N-nitrosobis(trifluoromethyl)amine as a predominant product probably proceeded by the same mechanisms as those described for the reactions involving tris(trifluoromethyl)phosphine and O-nitrosobis-(trifluoromethyl)hydroxylamine. The presence of perfluoro-2-azapropene carbonyl fluoride and the polymer $(CF_3AsO_2)_n$, can be explained by the following reaction pathway:



$$(CF_3)_2\overset{O}{\overset{\|}{As}}ON(CF_3)_2 \longrightarrow (CF_3)_2AsO_2 + (CF_3)_2N \xrightarrow{SiO_2} CF_3N{=}CF_2$$



$$\begin{tikzcd}(CF_3)_2AsO_2 \arrow[r] & CF_3AsO_2 \arrow[d] & + & CF_3 \arrow[d] \\ & \frac{1}{n}(CF_3AsO_2)n & & COF_2\end{tikzcd}$$

Reactions with tris(trifluoromethyl)stibine

The reactions of 0-nitrosobis(trifluoromethyl)hydroxylamine with equimolar tris(trifluoromethyl)stibine proceeded smoothly at room temperature. After ten hours, the 0-nitrosobis(trifluoromethyl)hydroxylamine was consumed completely but 25% of the tris(trifluoromethyl)stibine was recovered

Tri[bis(trifluoromethyl)nitroxy]stibine, $[(CF_3)_2NO]_3Sb$ (III) was obtained in 46.5% yield, based on the amount of 0-nitrosobis(trifluoromethyl)hydroxylamine used. The compound (III) is a white hygroscopic solid at room temperature, and it is not volatile enough for the infrared spectrum of the vapour to be recorded. The identity of compound (III) was determined by its reaction with excess hydrogen chloride, from which three moles of N,N-bis(trifluoromethyl)hydroxylamine was obtained in 99% yield. The other product obtained was antimony trichloride, as shown by the equation:

$$[(CF_3)_2NO]_3Sb + 3HCl \longrightarrow 3(CF_3)_2NOH + SbCl_3$$

Alkaline hydrolysis of compound (III) did not yield any trifluoromethane.

The other product obtained from the reaction with tris(trifluoromethyl)stibine was di[bis(trifluoromethyl)nitroxy]trifluoromethylstibine, $[(CF_3)_2NO]_2SbCF_3$(IV). The yield was 26%, based on the amount of 0-nitrosobis(trifluoromethyl)hydroxylamine used. Compound (IV) is a stable colourless liquid at room temperature. It is readily hydrolysed in air to give N,N-bis(trifluoromethyl)hydroxylamine.

With anhydrous hydrogen chloride, compound (IV) liberated quantitatively two moles of N,N-bis(trifluoromethyl)hydroxylamine. The other volatile product was dichlorotrifluoromethylstibine, obtained in 12% yield. The non-volatile product was antimony trichloride. The formation of antimony trichloride is presumably due to the disproportionation of dichlorotrifluoromethylstibine as shown below:

$$2CF_3SbCl_2 \longrightarrow (CF_3)_2SbCl + SbCl_3$$

Alkaline hydrolysis of compound (IV) by 20% aqueous sodium hydroxide gave one mole of trifluoromethane.

In the reactions of O-nitrosobis(trifluoromethyl)hydroxylamine and tris(trifluoromethyl)stibine, all the products were identified and isolated quantitatively. A material balance of the equation can be written as follows:

$$\underset{3.31\ \text{mmoles}}{(CF_3)_2NONO} + \underset{2.47\ \text{mmoles}}{(CF_3)_3Sb} \longrightarrow \underset{1.54\ \text{mmoles}}{[(CF_3)_2NO]_3Sb} + \underset{0.86\ \text{mmoles}}{[(CF_3)_2NO]_2SbCF_3}$$

By calculating the amounts of O-nitrosobis(trifluoromethyl)-hydroxylamine and tris(trifluoromethyl)stibine reacted, the relative amounts of the bis(trifluoromethyl)nitroxy and trifluoromethyl groups are shown below:

Total number of moles	Reactants (mmoles)	Products (mmoles)
i) $(CF_3)_2NO$ group	3.31	6.34
ii) CF_3 group attached to Sb only	7.41	0.86
iii) CF_3 group attached to Sb and N	14.03	13.54
iv) Sb (atom)	2.47	2.40

From the table, it is noted that an additional 3.03 mmoles of bis(trifluoromethyl)nitroxy groups are attached to Sb(III) derivatives, namely tri[bis(trifluoromethyl)nitroxy]stibine and di[bis(trifluoromethyl)nitroxy]trifluoromethylstibine. These reactions can be rationalised in terms of free radical mechanisms. The formation of the trifluoromethyl radicals can be explained by the homolytic cleavage of the CF_3-Sb bond of the intermediate $(CF_3)_2NOSb(CF_3)_3$ radicals. The attack of nitric oxide by the trifluoromethyl radical afforded trifluoronitrosomethar which, on further attack by another trifluoromethyl radical, gives bis-(trifluoromethyl)nitroxyl. The mechanistic pathways leading to the formation of the antimony derivatives are shown as follows:

$$(CF_3)_2NONO \longrightarrow (CF_3)_2NO + NO$$

$$(CF_3)_3Sb + (CF_3)_2NO \longrightarrow (CF_3)_3SbON(CF_3)_2$$

$$(CF_3)_3SbON(CF_3)_2 \longrightarrow (CF_3)_2SbON(CF_3)_2 + CF_3$$

$$CF_3 + NO \longrightarrow CF_3NO$$

$$CF_3NO + CF_3 \longrightarrow (CF_3)_2NO$$

$$(CF_3)_2NO + NO \longrightarrow (CF_3)_2NONO$$

$$(CF_3)_2SbON(CF_3)_2 + (CF_3)_2NO \longrightarrow (CF_3)_2Sb[ON(CF_3)_2]_2$$

$$(CF_3)_2Sb[ON(CF_3)_2]_2 \longrightarrow CF_3Sb[ON(CF_3)_2]_2 + CF_3$$

$$CF_3Sb[ON(CF_3)_2]_2 + (CF_3)_2NO \longrightarrow CF_3Sb[ON(CF_3)_2]_3$$

$$CF_3Sb[ON(CF_3)_2]_3 \longrightarrow [(CF_3)_2NO]_3Sb + CF_3$$

A concomitant mechanism which appears possible is that involving the pentavalent antimony intermediate followed by an elimination of trifluoronitrosomethane, similar to those proposed for the above analogous phosphorus and arsenic reactions.

OBSERVATIONS

From the foregoing sections involving the reactions between O-nitrosobis(trifluoromethyl)hydroxylamine and tris(trifluoromethyl)phosphine, arsine and stibine, several interesting features emerge.

The production of the bis(trifluoromethyl)nitroxy derivatives of phosphorus, arsenic and antimony can be attributed to the ease of cleavage of the $(CF_3)_2NO{-}NO$ bond. This kind of situation can lead to two types of intermediates, namely the quadrivalent $(CF_3)_2NOM(CF_3)_3$ and the pentavalent $(CF_3)_2NOM(CF_3)_3(NO)$, where M = P, As and Sb. They will then undergo reductive elimination process to give the corresponding trivalent bis(trifluoromethyl)nitroxy derivatives, as shown below:

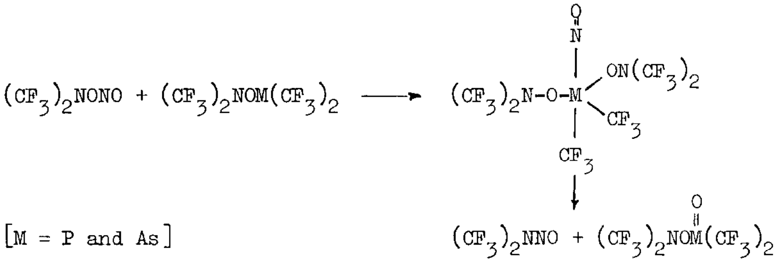
$$\begin{tikzcd}
(CF_3)_2NONO + (CF_3)_3M \arrow[r] & (CF_3)_2NOM(CF_3)_3NO \arrow[d] \\
 & (CF_3)_2NOM(CF_3)_2 + CF_3NO
\end{tikzcd}$$

and

$$\begin{tikzcd}
(CF_3)_3M + (CF_3)_2NO \arrow[r] & (CF_3)_2NOM(CF_3)_3 \arrow[d] \\
 & (CF_3)_2NOM(CF_3)_2 + CF_3
\end{tikzcd}$$

In the case of tris(trifluoromethyl)stibine, the above reaction can proceed further by a step-wise oxidative addition followed by elimination reactions, leading eventually to the formation of $[(CF_3)_2NO]_3Sb$.

However, it has been found that with phosphorus and arsenic compounds, no corresponding $[(CF_3)_2NO]_3M$ (where M = P and As) were produced. The reactions were more complex, as phosphorus and arsenic have greater tendency to form the M=O bonds as shown below:



$$(CF_3)_2NONO + (CF_3)_2NOM(CF_3)_2 \longrightarrow (CF_3)_2N\text{-}O\text{-}\overset{\overset{O}{\overset{\|}{N}}}{\underset{CF_3}{M}}\begin{smallmatrix}ON(CF_3)_2\\CF_3\end{smallmatrix}$$

$$\downarrow$$

$$(CF_3)_2NNO + (CF_3)_2NO\overset{O}{\overset{\|}{M}}(CF_3)_2$$

[M = P and As]

The above reactions of phosphorus and arsenic compounds lead to the formation of N-nitrosobis(trifluoromethyl)amine which appeared as the predominant product.

The complete absence of N-nitrosobis(trifluoromethyl)amine in the reactions with $(CF_3)_3Sb$ is because antimony has less tendency to undergo de-oxygenation reaction. Instead, the quadrivalent antimony intermediate, $[(CF_3)_2NO]_2Sb(CF_3)_2$, that is formed, affords the trifluoromethyl radical which then attacks the trifluoronitrosomethane to give bis(trifluoromethyl)-nitroxyl as shown below:

$$(CF_3)_2NOSb(CF_3)_2 + (CF_3)_2NO \longrightarrow [(CF_3)_2NO]_2Sb(CF_3)_2$$

$$\downarrow$$

$$[(CF_3)_2NO]_2SbCF_3 + CF_3$$

$$CF_3NO + CF_3 \longrightarrow (CF_3)_2NO$$

These reactions are novel and account for the additional amount of bis(trifluoromethyl)nitroxy groups attached to antimony, above what were derived from $(CF_3)_2NONO$.

The presence of a small amount of carbonyl fluoride and perfluoro-2-azapropene in the reactions with $(CF_3)_3As$ is presumably because the arsenic derivative, $(CF_3)_2NOAs(O)(CF_3)_2$, being unstable undergoes decomposition to form CF_3 and $(CF_3)_2N$ radicals. The radicals in turn attack the glass ampoul to give the corresponding COF_2 and $CF_3N{=}CF_2$. These explanations are consistent with the findings of Haszeldine and Dinwoodie [2].

EXPERIMENTAL

Infrared spectra (4000 - 400 cm^{-1}) were determined with a Perkin Elmer 337 Grating Infrared Spectrophotometer. Tris(trifluoromethyl)-phosphine, arsine and stibine were prepared by reacting trifluoroiodomethane with phosphorus, arsenic and antimony at elevated temperatures [13, 14, 15]. O-Nitrosobis(trifluoromethyl)hydroxylamine was prepared by reacting nitrosyl chloride with mercury di[bis(trifluoromethyl)nitroxide] [16]. Vapour pressures of new compounds were measured in vacuo using a spiral gauge.

Reaction of tris(trifluoromethyl)phosphine with O-nitrosobis(trifluoromethyl)hydroxylamine

Tris(trifluoromethyl)phosphine (0.6043 g, 2.54 mmoles) and O-nitrosobis(trifluoromethyl)hydroxylamine (0.5058 g, 2.55 mmoles) were sealed together in a Pyrex glass ampoule. The ampoule was placed in ethanol-dry ice mixture (-78°C) and allowed to warm slowly to room temperature. No reaction was observed. The mixture was then heated at 65°C in an oven for 30 hours. The colour of the hydroxylamine still remained. When the ampoule was chilled in liquid air, a small quantity of blue solid was observed together with the reddish-orange colour of the hydroxylamine.

To accelerate the reaction, the ampoule was heated to 85°C for another twenty-four hours. By then the reddish-orange colour of the O-nitrosobis(trifluoromethyl)hydroxylamine was completely discharged. A greenish-yellow gas, which solidified to a clear, greenish solid in liquid air, remained in the ampoule. The product mixture was separated by trap-to-trap distillation. The following fractions were obtained:

i) A colourless liquid, trapped at -78°C (passed the -40°C trap), gave 0.1190 g (0.34 mmole; 54.0% based on the amount of phosphine reacted). The liquid was identified as bis(trifluoromethyl)nitroxybis(trifluoromethyl)phosphine oxide. It was sensitive to air and decomposed to give a heavy, non-volatile colourless liquid. The infrared spectrum of this fraction together with its assignment are summarised in Table 1, and the vapour pressure measurements are given in Table 2.

ii) The unreacted tris(trifluoromethyl)phosphine (0.4535 g, 1.91 mmoles, 75.0% recovery) was trapped at -96°C (passed the -78°C).

iii) A greenish-yellow liquid was trapped at -120°C (passed the -96°C trap) and gave bands in the infrared spectrum very similar to N-nitrosobis(trifluoromethyl)amine. The bands of the infrared spectrum are located at 1625m, 1420vs, 1360vs, 1320vs, 1215vs, 1020vs, 925w, 780w, and 620w cm^{-1}. The yield was 0.3729 g (2.05 mmoles; 80% based on the amount of hydroxylamine used). Analysis gave: mol. wt., 182; F, 62.2%. $C_2F_6N_2O$ requires mol. wt., 182; F, 62.4%.

iv) A mixture of greenish-yellow, white and blue condensate was trapped at -196°C (0.1200 g). A ring of blue condensate appeared at the arm of the fractionation trap, resembling that of trifluoronitrosomethane. However, the volatile mixture could not be fractionated. In the infrared spectrum, the intense bands due to the carbonyl fluoride appeared at 1970s, 1920s (doublet), 1620w, 1420s, 1320s, 1250-1230 (broad)vs, 1150w, 1090w, 1080w, 1020m, 975-960 (broad)w and 775m cm^{-1}.

v) A droplet of non-volatile, colourless liquid remained in the ampoule, too small to be characterised.

Reaction of bis(trifluoromethyl)nitroxybis(trifluoromethyl)phosphine oxide with chlorine

Bis(trifluoromethyl)nitroxybis(trifluoromethyl)phosphine oxide (0.0940 g, 0.27 mmole) was condensed with excess dry chlorine gas (0.0806 g, 1.14 mmoles) into a sealed glass ampoule. The ampoule was left at room temperature for four days. On fractionation, the unreacted compound and the chlorine gas were recovered quantitatively at -78°C and -196°C traps respectively.

Reaction of mercury(II)bis(trifluoromethyl)nitroxide and bis(trifluoromethyl)phosphinic chloride

Bis(trifluoromethyl)phosphinic chloride (0.5113 g , 2.32 mmoles) was condensed in vacuo into a pyrex glass ampoule containing the mercurial, $[(CF_3)_2NO]_2Hg$, which was formed by reacting excess bis(trifluoromethyl)-nitroxyl with mercury (0.3277 g).

The ampoule was sealed, shaken periodically, and left at room temperature for twenty hours. The liquid remained colourless but the solids turned from pale yellow to white, indicating that mercuric chloride had been formed. On fractionation, bis(trifluoromethyl)nitroxybis(trifluoromethyl)phosphine oxide was trapped as a colourless liquid at -78°C (passed -50°C) and it was the only volatile product. Yield: 0.7829 g, 2.22 mmoles; 96%, based on the amount of phosphinic chloride used. (Found: mol. wt., 355; F, 63.3%; P, 8.69%; calculated for $C_4F_{12}NO_2P$, mol. wt., 353; F, 64.6%, P, 8.78%). The infrared spectrum is identical to that given in Table 1.

Hydrolysis of bis(trifluoromethyl)nitroxybis(trifluoroethyl) phosphine oxide by 20% aqueous sodium hydroxide

Bis(trifluoromethyl)nitroxybis(trifluoromethyl)phosphine oxide (0.4074 g, 1.15 mmoles) was sealed with 10 ml of 20% sodium hydroxide in a glass ampoule. When the ampoule was left at room temperature for a few hours, the solution became slightly yellow. After twenty hours, the solution became clear again and some transparent solids were formed. The ampoule was then heated to 120°C for 24 hours. On fractionation, a volatile fraction, which passed the -126° trap, was collected. It was

Table 1. Infrared spectrum of $(CF_3)_2NOP(O)(CF_3)_2$

Peak (cm^{-1})	Intensity	Tentative Assignment
1345	m	P=O stretch
1322	vs	C-F stretch of CF_3N
1270	vs	
1239	vs	
1220	vs	
1210	vs	C-F stretch of CF_3P
1200	vs	
1150	sh	
1028	s	N-O stretch
970	m	C-N stretch
859	s	P-ON stretch
711	m	CF_3 symmetric deformation
612	w	
578	s	CF_3 asymmetric deformation
560	sh	
500	m	P=O bending
485	m	
460	m	

identified to be trifluoromethane (0 0807 g, 1 15 mmoles) from its infrared spectrum and molecular weight Thus only one more of trifluoromethane was liberated from one mole of $(CF_3)_2NOP(O)(CF_3)_2$.

Table 2. Vapour pressures of $(CF)_3)_2NOP(O)(CF_3)_2$

P(mm)	$\log_{10}P$(mm)	T(°C)	T(K)	$(^1/T)\times10^{-3}(K^{-1})$
32	1.5052	1	274	3.650
40	1.6021	5	278	3.597
45	1.6532	8	281	3.559
54.5	1.7364	11	284	3.521
64	1.8062	14	287	3.484
75.5	1.8780	17	290	3.448
88	1.9445	20	293	3.413
101	2.0043	23	296	3.378
111	2.0453	26	299	3.345
131	2.1173	29	302	3.3113
152	2.1810	32	305	3.2787

Vapour pressure measurements of $(CF_3)_2NOP(O)(CF_3)_2$ gave a straight line from 1°C to 32°C:

$$\log_{10}P(\mathrm{mm}) = 8.191 - \frac{1833}{T}$$

The following physical constants were obtained:

Latent heat of vaporization: 8.388 Kcal/mole

Extrapolated boiling point : 72.2°C

Trouton's constant : 24.30

Reactions of tris(trifluoromethyl)arsine with O-nitrosobis(trifluoromethyl)hydroxylamine

Tris(trifluoromethyl)arsine (1.0227 g. 3.63 mmoles) and O-nitrosobis-(trifluoromethyl)hydroxylamine (0.7239 g. 3.66 mmoles) were sealed in vacuo in pyrex glass ampoule of 100 ml capacity. The ampoule was left at room temperature for two days, but no reaction was observed. It was then put into the oven and the temperature was set progressively as follows: 40°C (12 hours) and 60°C (12 hours). There was still no reaction. Finally the oven temperature was set at 80°C. After two hours, a small quantity of white solid started to deposit on the walls of the ampoule and the reddish-orange colour of the hydroxylamine gradually changed to pale yellowish-green. After twenty-four hours of heating, besides the white solid, a mixture of gas and liquid, both yellowish-green in colour, remained in the ampoule.

After the removal of the volatile fractions, a white solid residue was left in the ampoule. When the ampoule was removed from the vacuum line and air was allowed into it, white fumes were formed inside the ampoule. 5 ml of 20% sodium hydroxide was then added into the ampoule and effervescence was observed immediately. The gas was later identified by its infrared spectrum to be trifluoromethane.

The volatile products gave the following fractions on fractionation:

i) A small amount of white solid (0.0934 g), called fraction (A), was trapped at -78°C (passed the -65° trap). When the solid was warmed up to room temperature, it melted to give two immiscible, colourless liquids. Despite repeated fractionations, the two immiscible liquids could not be separated. The infrared spectrum of this fraction showed absorptions at 1330vs, 1310vs, 1275vs, 1240vs, 1210vs, 1170s, 1155m, 1135vs, 1115m, 1100m, 1035m, 970m, 800w, 740s and 710s (broad) cm^{-1}.

(ii) Tris(trifluoromethyl)arsine (0.6089 g, 2.16 mmoles) was recovered at the -95°C trap (passed the -86°C trap). Recovery was 60%.

(iii) N-Nitrosobis(trifluoromethyl)amine (0.6457 g, 3.55 mmoles) was trapped as a yellowish liquid at the -126°C trap (passed the -95° trap). The yield was 97%, based on the amount of O-nitrosobis(trifluoromethyl)hydroxylamine used. It was identified by comparing the infrared spectrum with that of an authentic sample. The analysis of this fraction gave mol. wt. 183; C, 13.0%; F, 62.2%; $C_2F_6N_2O$ requires mol. wt. 182; C, 13.2%; F, 62.4%.

(iv) A blue mixture (0.2683 g) trapped at the -196°C trap (passed the -126°C trap). Only two compounds from this mixture, namely carbonyl fluoride and perfluoro-2-azapropene, were identified from the infrared spectrum of this fraction. The absorptions were located at 1970, 1940, 1920vs (triplet), 1800vs, 1430vs, 1390vs, 1370vs, 1350vs, 1320vs, 1290vs, 1270vs, 1250vs, 1205s, 1150m, 1010-1000s (doublet), 955m, 775s and 730m cm^{-1}. The blue colour was probably due to trifluoronitrosomethane.

<u>Reaction of fraction (A) with anhydrous hydrogen chloride</u>

0.0237 g of fraction (A) was sealed in vacuo with excess anhydrous hydrogen chloride (0.0773 g, 2.12 mmoles) in a glass ampoule. The ampoule was left at room temperature for two days. Fractionation of the products gave the following fractions:

i) a colourless liquid (0.0058 g), trapped at -65°C. It did not give any infrared absorption band.

ii) N,N-bis(trifluoromethyl)hydroxylamine (0.0049 g, 0.029 mmole) trapped at -95° trap (passed the -65°C trap).

iii) chlorobis(trifluoromethyl)arsine (0.0032 g, 0.013 mmoles), trapped at -120°C (passed the -95°C trap). The infrared spectrum was identical to that of an authentic sample, with absorptions located at 1205vs, 1060vs, 1039vs, 1114sh, 1108vs and 730 cm^{-1}.

iv) excess anhydrous hydrogen chloride (0.0080 g, 0.22 mmoles), recovered at the -196°C trap.

Reaction of fraction (A) with 20% acqueous sodium hydroxide

0.0337 g of fraction (A) was sealed in vacuo with 5 ml 20% aqueous sodium hydroxide in a glass ampoule. The ampoule was heated to 120°C for one night. On fractionation of the mixture, trifluoromethane (0.0059 g, 0.08 mmole) was obtained as the only volatile product.

Reactions with tris(trifluoromethyl)stibine with O-nitrosobis(trifluoromethyl)hydroxylamine

Tris(trifluoromethyl)stibine (1.0819 g, 3.29 mmoles) and O-nitrosobis(trifluoromethyl)hydroxylamine (0.6553 g, 3.31 mmoles) were condensed in vacuo into a pyrex glass ampoule of 75 ml capacity. The sealed ampoule was allowed to stand at room temperature for 10 hours. By then the colour of the O-nitrosobis(trifluoromethyl)hydroxylamine was completely discharged. Some white crystalline solid and a small amount of colourless liquid remained in the ampoule.

Fractionation of the products gave the following fractions:

i) A white crystalline solid, trapped at 0°C (0.9629 g, 1.54 mmoles); 46.5% yield based on the amount of the hydroxylamine used). It was identified as tri[bis(trifluoromethyl)nitroxy]stibine, $[(CF_3)_2NO]_3Sb$. The compound was a white solid at room temperature, just volatile enough to be distilled into the vacuum line, but not volatile enough for a vapour phase infrared spectrum to be taken, and was too hygroscopic for a satisfactory nujol mull to be made. (Analysis: found, C, 11.01%; $C_8F_{18}N_3O_3Sb$ requires C, 11.51%).

ii) A white crystalline solid, trapped at -130°C (passed 0°C trap). The solid melted into a colourless liquid at room temperature and was identified to be di[bis(trifluoromethyl)nitroxy]trifluoromethylstibine. (0.4540g, 0.86 mmole, 26% yield, based on the amount of the hydroxylamine used.) The infrared spectrum is given in Table 3.

iii) Unreacted tris(trifluoromethyl)stibine (0.2694 g, 0.82 mmoles, 25% recovery) was recovered at the -83°C trap (passed the -65°C. trap).

Reaction of tri[bis(trifluoromethyl)nitroxy]stibine with 20% aqueous sodium hydroxide

0.3194 g of the tri[bis(trifluoromethyl)nitroxy]stibine was allowed to react with 10 ml of 20% sodium hydroxide at room temperature for 4 days. The reactants were sealed in a glass ampoule. On fractionation, no trifluoromethane was liberated. The solution was then acidified with hydrochloric acid and on bubbling gaseous hydrogen sulphide into the solution, a reddish-orange precipitate of antimony pentasulphide was formed. This showed that it was an antimony compound and no trifluoromethyl group was attached to the antimony.

Reaction of tri[bis(trifluoromethyl)nitroxy]stibine with excess anhydrous hydrogen chloride

At room temperature, tri[bis(trifluoromethyl)nitroxy]stibine (0.2400 g, 0.38 mmole) reacted with excess anhydrous hydrogen chloride to give bis(trifluoromethyl)hydroxylamine quantitatively (0.1903 g, 1.13 mmoles, 99.1% yield). The bis(trifluoromethyl) hydroxylamine was the only volatile product and was identified from its infrared spectrum. The other product was the white deliquescent antimony trichloride which was left in the ampoule. (Analysis: found, Cl, 46.7%; $SbCl_3$requires Cl, 46.6%).

Reaction of di[bis(trifluoromethyl)nitroxy]trifluoromethylstibine with 20% aqueous sodium hydroxide

Di[bis(trifluoromethyl)nitroxy]trifluoromethylstibine (0.1114 g, 0.22 mmole) was hydrolysed by 5 ml of 20% sodium hydroxide at room temperature for 4 days. The only volatile product obtained was trapped at -196°C (passed -126°C trap). It was found to be trifluoromethane (0.0154 g, 0.22 mmole).

The remaining solution was acidified with hydrochloric acid, and on passing gaseoùs hydrogen sulphide, a reddish-orange precipitate appeared, showing that antimony was present.

Reaction of di[bis(trifluoromethyl)nitroxy]trifluoromethylstibine with anhydrous hydrogen chloride

Di[bis(trifluoromethyl)nitroxy]trifluoromethystibine (0.1803 g, 0.34 mmole) was allowed to react with hydrogen chloride (0.0683 g, 1.87 mmoles) at room temperature in a pyrex glass ampoule.

On fractionation, the fraction trapped at -83°C (passed the -65°C trap) was identified by its infrared spectrum to be N,N-bis(trifluoromethyl) hydroxylamine. The yield was quantitative (0.1141 g, 0.68 mmole), showing that two moles of N,N-bis(trifluoromethyl)hydroxylamine were liberated from one mole of the antimony(III) derivative.

A white solid (0.0117 g, 0.04 mmole, 12% yield) trapped at the -30°C trap was identified as dichlorotrifluoromethylstibine, (Found: Cl, 26.22%, CF_3Cl_2Sb requires Cl, 27.10%). The white solid was not volatile enough to give a gas-phase infrared spectrum.

A small quantity of white, hydroscopic residue (0.0790 g) was left in the ampoule. (Analysis: Cl, 46.0%; $SbCl_3$ requires Cl, 46.6%). It was regarded as antimony trichloride.

Table 3: Infrared spectrum of $[(CF_3)_2NO]_2SbCF_3$

Absorption cm^{-1}	Intensity	Tentative Assignment
1330	m	
1305	vs	C-F stretch of CF_3-N
1265	vs	
1235	vs	
1215	sh	
1190	sh	C-F stretch of CF_3-Sb
1168	m	
1140	m	
1118	s	
1030	s	N-O stretch
971	s	C-N stretch
960	sh	
790	m	Sb-ON stretch
735	w	
710	s	CF_3 deformation
685	w	
558	w	

Excess hydrogen chloride (0.0421 g, 1.2 mmoles) was recovered at the -196°C trap (passed the -120°C trap). The infrared spectrum of this fraction indicated the presence of a small quantity of unidentified compounds with absorptions at 1150sh, 1130m, 1115vs, 1105s, 1036vs, 1030vs and 820, 808, 800m (triplet) cm^{-1}.

REFERENCES

1 J. Jander & R.N. Haszeldine, J. Chem. Soc. (1954) 699.

2 A.H. Dinwoodie & R.N. Haszeldine, J. Chem. Soc. (1965) 1675.

3 W.D. Blackley & R.R. Reinhard, J. Am. Chem. Soc. 87 (1965) 802.

4 R.E. Banks, W.M. Chong, R.N. Haszeldine & G. Shaw, J. Chem. Soc. (C), (1970) 55.

5 R.N. Haszeldine & B.J.H. Mattinson, J. Chem. Soc. (1957) 1741.

6 M.D. Vorob'ev, A.S. Filatov & M.A. Englin, Zh. Obshch. Khim, 44 (12) (1974) 2724.

7 A.H. Dinwoodie & R.N. Haszeldine, J. Chem. Soc (A), (1969), 431.

8 J.A. Young, S.N. Tsoukalas and R.D. Dresdner, J. Am. Chem. Soc. 82 (1960) 396.

9 H.G. Ang & W.S. Lien, J. Fluorine Chem. 11 (1978) 419.

10 R.C. Dobbie, J.Chem. Soc. (A), (1971) 2874.

11 H.G. Ang & K.F. Ho, J. Organometal. Chem. 19, (1969), P 19.

12 H.G. Ang & K.F. Ho, J. Organometal. Chem. 27, (1971), 349.

13 F.W. Bennett, H.J. Emeléus & R.N. Haszeldine, J. Chem. Soc. (1953) 1

14 G.R.A. Brandt, H.J. Emeléus & R.N. Haszeldine, J. Chem. Soc. (1952) 2552.

15 J.W. Dale, H.J. Emeléus, R.N. Haszeldine & J.H. Moss, J. Chem. Soc. (1957) 3708.

16 H.J. Emeléus, J.M. Shreeve & P.M. Spaziante, Chem. Commun. (1968) 1252; and J. Chem. Soc. (A) (1969) 431.