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REACTIONS OF BIS(TRIFLUOROMETHYL)NITROXYL WITH $(CF_3)_3M$ (M=P, Sb) AND
PROPERTIES OF BIS(TRIFLUOROMETHYL)NITROXY DERIVATIVES OF P, As and Sb

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SUMMARY

Bis(trifluoromethyl)nitroxyl gives an oxidative addition reaction with tris(trifluoromethyl)phosphine and radical exchange reactions with stibine. The mechanisms of the above reactions and the properties of bis(trifluoromethyl)nitroxy derivatives of phosphorus, arsenic and antimony are discussed.

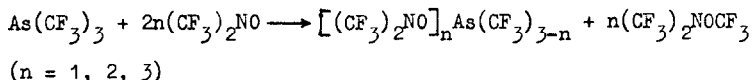
INTRODUCTION

In recent years, several papers have appeared showing interesting reactions between bis(trifluoromethyl)nitroxyl and compounds of Group V elements. Reactions with phosphorus trichloride yield two products, namely, $(CF_3)_2NOPCl_4$ and $(CF_3)_2NOPCl_2$ [1]. On the other hand, phosphorus trifluoride yields $(CF_3)_2NON(CF_3)_2$, POF_3 and $[(CF_3)_2NO]_2PF_3$ [2]. Displacement of iodine occurs with $(CF_3)_2PI$ to give $(CF_3)_2PON(CF_3)_2$ [3]. The latter can also be obtained from $(CF_3)_2PH$ since bis(trifluoromethyl)-nitroxyl is both a powerful hydrogen abstractor and a radical scavenger [4]. Reactions of the nitroxyl are extended to trifluoromethyl-substituted compounds of Group V elements.

RESULTS AND DISCUSSION

It has recently been shown that tris(trifluoromethyl)arsine undergoes stepwise group exchange reactions with bis(trifluoromethyl)-nitroxyl to form mono-, di- and tri-bis(trifluoromethyl)nitroxy arsenic

derivatives, $[(CF_3)_2NO]_nAs(CF_3)_{3-n}$ ($n = 1, 2, 3$), and tris(trifluoromethyl)hydroxylamine according to the equation (5, 6):



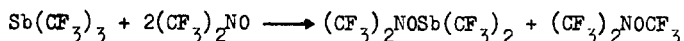
In our hands, it is found that a stoichiometric mixture of tris(trifluoromethyl)phosphine and bis(trifluoromethyl)nitroxyl interacts at room temperature to give di-[bis(trifluoromethyl)nitroxy]tris(trifluoromethyl)phosphorane, $[(CF_3)_2NO]_2P(CF_3)_3$ (I), confirmed by its fluorine analysis and infrared spectrum. No exchange reaction is found under the condition of the experiment, which is distinctly different from the reaction with $[(CH_3)_2N]_3P$ since $[(CH_3)_2N]_2PON(CF_3)_2$ and $(CF_3)_2NON(CH_3)_2$ are formed [7].

The phosphorane (I) is a colourless liquid. On hydrolysis with 20% sodium hydroxide at 120° for 48 hours, fluoroform is eliminated in 80.5% yield.

^{19}F nuclear magnetic resonance spectrum of the phosphorane (I) gives a resonance at +68 ppm w.r.t. trichlorofluoromethane, and is due to the presence of bis(trifluoromethyl)nitroxy group. A broad peak which could be attributed to the trifluoromethyl groups bonded to phosphorus is also observed.

Compound (I) is unstable at elevated temperatures. On heating at $80^\circ C$, a heavy liquid was obtained which could be assigned as $[(CF_3)_2NO]_4PCF_3$. Another compound which was isolated and identified was tris(trifluoromethyl)hydroxylamine.

At $-74^\circ C$, the reaction between tris(trifluoromethyl)stibine and bis(trifluoromethyl)nitroxyl in the ratio of 1:2 proceeds smoothly according to the following equation:



[Bis(trifluoromethyl)nitroxy]bis(trifluoromethyl)stibine (II) is a colourless liquid which can be trapped at $-65^\circ C$ under vacuum. Its

structure is established by the reaction with 20% sodium hydroxide solution which yields two moles of fluoroform, as well as its reaction with anhydrous hydrogen chloride which gives a quantitative yield of bis(trifluoromethyl)hydroxylamine. The latter reaction indicates the relative ease of cleaving the Sb-O bond as shown by the equation:



Confirmation of the structure of compound (II) is obtained from its infrared spectrum.

Compound (II) is stable at -30°C . On standing at room temperature, it gives an intractable non-sublimable white solid (III), perfluoro-2-azapropene, trifluoromethylisocyanate and silicon tetrafluoride. The last three compounds are trapped together as a mixture at liquid air temperature, and their presence are confirmed by their infrared spectra [8, 9]. The white solid does not react with anhydrous hydrogen chloride, indicating the bis(trifluoromethyl)nitroxy group is not present. It is hydrolysed easily by 20% sodium hydroxide solution to yield fluoroform. The infrared spectrum of solid (III) contains one broad-to-strong peak in the range 1115 to 1135 cm^{-1} , which can be assigned to the C-F stretching vibrations of trifluoromethyl group bonded directly to antimony [10]. The above reactions together with the infrared spectrum of (III) establish the presence of trifluoromethyl group directly bonded to antimony, and the absence of bis(trifluoromethyl)nitroxy group. Evidence for the presence of $\text{Sb}=\text{O}$ in solid (III) is derived from the peak of moderate intensity located at 665 cm^{-1} in its infrared spectrum [11 - 14]. Difficulties are encountered in establishing its composition because of its ease of hydrolysis in air.

The reaction between the nitroxyl radical and tris(trifluoromethyl)-stibine in the ratio of 4:1 at 70°C produces a complete discharge of the coloured radical. On warming to room temperature, a white solid (IV) precipitates and the other volatile products that are identified are perfluoro-2-azapropene, trifluoromethylisocyanate and silicon tetrafluoride.

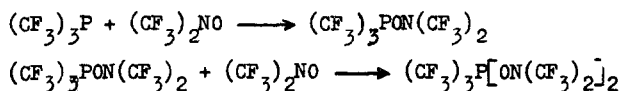
Extension of the reaction using 6:1 molar ratio also produces a white solid (V) and similar volatile products. In this case, the purple colour due to the radical is not completely discharged.

products, bis(trifluoromethyl)nitroxyl gives only addition compound [16, 17, 18]. The latter reaction illustrates the similarity in property between bis(trifluoromethyl)nitroxyl and chlorine which also gives an addition product, $(\text{CF}_3)_3\text{PCl}_2$ [19]. Such a similarity has also been exhibited in their reactions with selenium or tellurium [20].

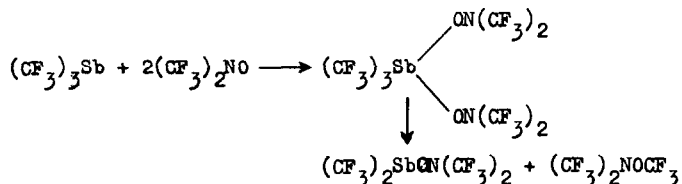
Unlike the reactions involving tris(trifluoromethyl)arsine with methyl iodide or N-halogenobis(trifluoromethyl)amine, the reactions between tris(trifluoromethyl)arsine and bis(trifluoromethyl)nitroxyl give not only mono- and di-substituted derivatives, $[(\text{CF}_3)_2\text{NO}]_n\text{As}(\text{CF}_3)_{3-n}$ ($n = 1, 2$), but also proceed a stage further to afford the tri-substituted derivative, $\text{As}[\text{ON}(\text{CF}_3)_2]_3$, even at moderate temperatures.

Tris(trifluoromethyl)stibine does not react with methyl iodide. On the other hand, the nature of reactions of N-halogenobis(trifluoromethyl)amine and bis(trifluoromethyl)nitroxyl with tris(trifluoromethyl)stibine is different since no bis(trifluoromethyl)amino-derivatives of antimony have been isolated even at low temperatures.

The mechanism of addition to $(\text{CF}_3)_3\text{P}$ is probably a step-wise free radical addition:

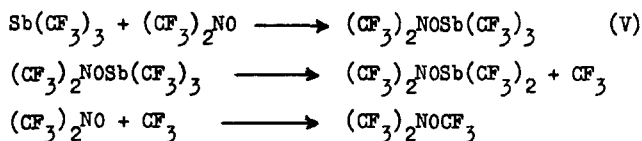


Substitution reactions with the arsenic and antimony analogues can proceed via addition followed by elimination reactions. For example,



The formation of the four co-ordinate radical intermediate (V) cannot be eliminated since trifluoromethyl radical can be easily released to afford the antimony derivative, $(\text{CF}_3)_2\text{NOSb}(\text{CF}_3)_2$. The formation of only tris(trifluoromethyl)hydroxylamine instead of hexafluoroethane

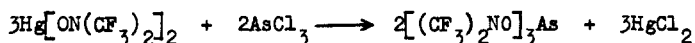
indicates that the rate of scavenging of the trifluoromethyl radical by the nitroxyl is much faster than the rate of coupling of trifluoromethyl radicals. The reactions can be represented by the following equations:



It is not unlikely that the reaction of bis(trifluoromethyl)nitroxyl with tris(trifluoromethyl)stibine proceeds both via a pentacovalent intermediate as well as an antimony radical intermediate (V).

Properties of Arsenic Derivatives

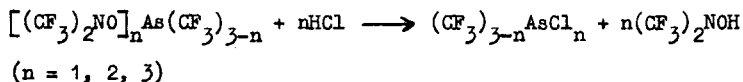
The yield of tri[bis(trifluoromethyl)nitroxy]arsine arising from the reaction of bis(trifluoromethyl)nitroxyl with tris(trifluoromethyl)arsine or arsenic metal, or from the interaction of di[bis(trifluoromethyl)nitroxy]mercury with arsine is usually very low [15, 21]. It has now been prepared in better yields (~ 75%) by the reaction of di[bis(trifluoromethyl)nitroxy]mercury with arsenic trichloride in an inert polyhalogeno solvent,



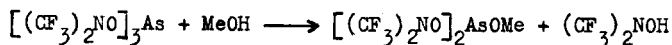
Thus, this method is adopted in the preparation of tri[bis(trifluoromethyl)nitroxy]arsine for further study of its properties.

The mono- and di-bis(trifluoromethyl)nitroxy arsenic derivatives are liquids at room temperature, while the tri[bis(trifluoromethyl)nitroxy]arsine is a colourless crystalline solid which melts at 29.5°C. They are all susceptible to attack by moisture. Hydrolysis with sodium hydroxide solution releases fluoroform from the mono- and di-derivatives.

The mono-, and di- and tri-substituted arsenic derivatives remain unchanged despite heating at 120°C for 3 days. They react readily with excess anhydrous hydrogen chloride, cleaving the As-O bonds:



Tri[bis(trifluoromethyl)nitroxy]arsine interacts with methanol at room temperature to form di[bis(trifluoromethyl)nitroxy]methoxyarsine in 96.5% yield.



It is confirmed by the reaction with anhydrous hydrogen chloride which affords a quantitative yield of bis(trifluoromethyl)hydroxylamine and methoxydichloroarsine.



There was no reaction between di[bis(trifluoromethyl)nitroxy]-trifluoromethylarsine and trimethylsilane at room temperature. At 80°C for 5 days, however, a small amount of bis(trifluoromethyl)hydroxylamine is formed. Tri[bis(trifluoromethyl)nitroxy]arsine gives only a trace of bis(trifluoromethyl)hydroxylamine with trichlorosilane and dimethylchlorosilane.

The reaction of tri[bis(trifluoromethyl)nitroxy]arsine with trimethylstannane produces initially an orange solid which slowly turned black as the reaction continues. After 2 hours, fractionation in vacuo gives only a small amount of volatile products, bis(trifluoromethyl)-hydroxylamine being the major component.

Infrared spectra

The gas-phase infrared absorptions of bis(trifluoromethyl)nitroxy derivatives of phosphorus, arsenic and antimony give numerous intense bands at 1100 to 1350 cm^{-1} ; and these absorptions are generally ascribed to C-F stretching frequencies [22]. The bands appearing in the higher region from 1230-1350 cm^{-1} are due to the C-F stretching absorptions of bis(trifluoromethyl)nitroxy group(s) [23 - 25]. The frequencies in the lower region from about 1100 to 1250 cm^{-1} are ascribed to the C-F stretching vibrations of trifluoromethyl bonded directly to phosphorus, arsenic and antimony [18, 19, 26]. A strong peak at 1025-1030 cm^{-1} can be assigned to the N-O stretching vibration, while that at 970 cm^{-1} to the symmetric C-N-C skeletal stretching vibration. A new absorption of medium intensity which appears at about 855 cm^{-1} for the phosphorane and

800 cm^{-1} for the arsines and stibine (II) could be tentatively assigned as the M-ON(CF₃)₂ stretching vibration (M = P, As, Sb). Peaks in the 740-750 cm^{-1} region can be attributed to the symmetric C-N-C bonding mode, and those at 710-720 cm^{-1} to CF₃ deformation mode.

EXPERIMENTAL

Because many of the compounds handled are susceptible to hydrolysis and some also to oxidation, all manipulations were carried out in a vacuum system. Infrared spectra were recorded on Perkin Elmer 337 spectrometer.

Reaction of bis(trifluoromethyl)nitroxyl with tris(trifluoromethyl)phosphine

Tris(trifluoromethyl)phosphine (0.984 g., 4.13 mmoles) and bis(trifluoromethyl)nitroxyl (1.38 g., 8.22 mmoles) were sealed in a Pyrex ampoule under vacuum, and left to react overnight at room temperature. The next morning, the purple colour of bis(trifluoromethyl)nitroxyl radical was completely discharged. Vacuum fraction through five traps at temperatures ranging from 0°C to -196°C gave a colourless liquid at -20°C. It was identified to be di[bis(trifluoromethyl)nitroxy]tris(trifluoromethyl)phosphorane, [(CF₃)₂NO]₂P(CF₃)₃, (2.28 g., 3.97 mmoles; 96.1% yield based on the amount of phosphine used). Analysis:- Found: F, 69.50%; P, 5.32; calculated for C₇F₂₁N₂O₂P: F, 69.52%; P, 5.39. The vapour pressure over the range 34° to 65°C gave the equation $\log_{10} P(\text{mm}) = 7.44 - 1930/T$. The extrapolated b.p. was 149°C, the latent heat of vaporisation 8.83 kcal. mole⁻¹, and Trouton constant 20.9.

(a) Action of heat on [(CF₃)₂NO]₂P(CF₃)₃

Di[bis(trifluoromethyl)nitroxyl]tris(trifluoromethyl)phosphorane (1.23 g., 2.23 mmoles) was heated at 80°C in a sealed tube for 30 hours. Fractionation in vacuo gave the following fractions:-

(i) tetrakis[bis(trifluoromethyl)nitroxy]trifluoromethylphosphorane (0.744 g., 1.00 mmoles) at -20°C trap. Analysis:- Found: F, 66.4%; calculated for C₉F₂₇N₄O₄P: F, 66.45%;

(ii) tris(trifluoromethyl)hydroxylamine (0.481 g., 2.03 mmoles), passed -20°C trap, identified by its i.r. spectrum and molecular weight; and

(iii) an intractable heavy liquid in the reaction ampoule.

(b) Hydrolysis of $[(CF_3)_2NO]_2P(CF_3)_3$

Di[bis(trifluoromethyl)nitroxy]tris(trifluoromethyl)phosphorane (0.162 g., 0.282 mmoles) was hydrolysed by 30 ml of 20% sodium hydroxide solution at 120°C for 48 hours to give fluoroform (0.318 g., 0.454 mmoles).

Preparation of tri[bis(trifluoromethyl)nitroxy]arsine, $[(CF_3)_2NO]_3As$

Mercury (0.443 g., 0.0022 g. atom) was sealed with excess bis-(trifluoromethyl)nitroxyl (1.57 g., 9.35 mmoles) in a Pyrex ampoule with two break seals. The mixture was set aside to react at room temperature for three days. By this time, all the mercury was taken up in the purple liquid. Excess radical (0.843 g., 4.84 mmoles) was then removed under vacuum at room temperature to leave behind a colourless crystalline, needle-shape solid, di[bis(trifluoromethyl)nitroxy]mercury. About 3 ml of an inert polyhalogeno solvent, $CF_2ClCFCl_2$, was then added to the solid, and followed by the addition of arsenic trichloride (1.03 g., 5.68 mmoles). The resulting mixture was allowed to react at room temperature, with occasional shaking, for 2 days.

The volatile product was subjected to trap-to-trap fractional condensation in vacuo to give:-

- (i) a colourless, crystalline solid at -30°C trap, identified by its i.r. spectrum to be tri[bis(trifluoromethyl)nitroxy]-arsine; and
- (ii) the inert solvent -84°C trap.

A white solid which remained in the reaction vessel was identified as mercuric chloride.

Fraction (i) was further purified by fractionation, and tri[bis-(trifluoromethyl)nitroxy]arsine (0.651 g., 1.12 mmoles; 74.7% yield based on the amount of the nitroxyl radical consumed) was found at the -5°C trap.

The arsine derivative remained unchanged on heating at 120°C for 3 days. It reacted with excess anhydrous hydrogen chloride to give a quantitative yield of arsenic trichloride and bis(trifluoromethyl)hydroxylamine.

Reaction of $[(CF_3)_2NO]_3As$ with trimethylstannane

Tri[bis(trifluoromethyl)nitroxy]arsine (0.800 g., 1.38 mmoles) reacted very vigorously with trimethylstannane (0.252 g., 1.53 mmoles) at room temperature to give initially an orange solid which slowly turned black as the reaction continued. After 2 hours, the product was fractionated in vacuo to afford only a trace of bis(trifluoromethyl)-hydroxylamine. A black mass of solid remained behind in the reaction vessel.

Reaction of $[(CF_3)_2NO]_3As$ with methanol

Tri[bis(trifluoromethyl)nitroxy]arsine (1.56 g., 2.70 mmoles) was sealed with methanol (0.082 g., 2.56 mmoles) in a pyrex ampoule (30 ml); and the mixture was allowed to react at room temperature for 7 days. Vacuum fractionation yielded the following fractions:-

- (i) unreacted tri[bis(trifluoromethyl)nitroxy]arsine (0.070 g., 0.121 mmoles; 4.5% recovery) in the $-20^\circ C$ trap;
- (ii) a colourless liquid identified to be di[bis(trifluoromethyl)nitroxy]methoxyarsine (1.10 g., 2.49 mmoles; 96.5% yield based on the amount of $[(CF_3)_2NO]_3As$ reacted) in the $-45^\circ C$ trap; and
- (iii) bis(trifluoromethyl)hydroxylamine (0.430 g., 2.54 mmoles; 98.5% yield based on the amount of $[(CF_3)_2NO]_3As$ reacted).

Fraction (ii) was analysed by reacting it with anhydrous hydrogen chloride, which produced bis(trifluoromethyl)hydroxylamine quantitatively. The vapour pressure of $[(CF_3)_2NO]_2AsOCH_3$ over the range 12° to $100^\circ C$ was represented by $\log_{10} P(\text{mm}) = 7.25 - 1730/T$, giving an extrapolated b.p. of $122^\circ C$, latent heat of vaporisation of $7.89 \text{ kcal. mole}^{-1}$, and Trouton constant 20.

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

The reaction of di[bis(trifluoromethyl)nitroxy]methoxyarsine (1.10 g., 2.49 mmoles) with anhydrous hydrogen chloride (0.219 g., 6.00

mmoles) at room temperature for 4 days produced, on vacuum fractionation, the following fractions:

- (i) a colourless liquid at -50°C trap which was identified to be methoxydichloroarsine (0.425 g., 2.40 mmoles; 96.4% yield based on the amount of arsine reacted). Analysis:- Found: Cl, 40.00%; calculated for $\text{CCl}_2\text{H}_3\text{AsO}:\text{Cl}$, 40.12%;
- (ii) a quantitative yield of bis(trifluoromethyl)hydroxylamine (0.836 g., 4.95 mmoles; 99.4% yield based on the amount of the arsine reacted); and
- (iii) unreacted hydrogen chloride

The vapour pressure measurement of $\text{CH}_3\text{OAsCl}_2$ over a range 23° to 73°C gave an equation $\log_{10} P(\text{mm}) = 9.57 - 2380/T$. The extrapolated b.p. was 83°C .

Reactions of $[(\text{CF}_3)_2\text{NO}]_3\text{As}$ with trichlorosilane and dimethylchlorosilane

A mixture of tri[bis(trifluoromethyl)nitroxy]arsine (0.680 g., 1.17 mmoles) and trichlorosilane (0.158 g., 1.17 mmoles) was allowed to react in a sealed ampoule at room temperature for two days. The reaction afforded only a trace of bis(trifluoromethyl)hydroxylamine.

A similar observation was obtained in the reaction of tri[bis(trifluoromethyl)nitroxy]arsine with dimethylchlorosilane.

Reaction of $(\text{CF}_3)_2\text{NOAs}(\text{CF}_3)_2$ with hydrogen chloride

$(\text{CF}_3)_2\text{NOAs}(\text{CF}_3)_2$ (0.401 g., 1.05 mmoles) reacted with hydrogen chloride (0.045 g.) at 100°C for a day to afford bis(trifluoromethyl)chloroarsine (0.255 g., 1.03 mmoles) trapped at -60°C and bis(trifluoromethyl)hydroxylamine (0.170 g., 1.01 mmoles) trapped at -84°C . The products were identified by their i.r. spectra.

Reaction of $[(\text{CF}_3)_2\text{NO}]_2\text{AsCF}_3$ with hydrogen chloride

The interaction of di[bis(trifluoromethyl)nitroxy]trifluoromethylarsine (0.373 g., 0.777 mmoles) with hydrogen chloride (0.061 g., 1.67 mmoles) at 100°C for 1 day afforded the following fractions:-

- (i) trifluoromethyldichloroarsine (0.106 g., 0.493 mmoles) at -60°C trap. Analysis:- Found: Cl, 32.86%; calculated for $\text{CF}_3\text{Cl}_2\text{As}$; Cl, 33.01%;
- (ii) a mixture of trifluoromethyldichloroarsine and bis(trifluoromethyl)hydroxylamine (0.292 g.) at -84°C trap, and identified by its i.r. spectrum; and
- (iii) excess hydrogen chloride (trace) at liquid air trap.

The i.r. spectrum of trifluoromethyldichloroarsine contains only two intense peaks at 1187 cm^{-1} and 1134 cm^{-1} which are ascribed to the C-F stretching frequencies.

Reactions of bis(trifluoromethyl)nitroxyl with tris(trifluoromethyl)stibine

(a) With two moles of bis(trifluoromethyl)nitroxyl

Tris(trifluoromethyl)stibine (0.392 g., 1.19 mmoles) and bis(trifluoromethyl)nitroxyl (0.406 g., 2.42 mmoles) in a 1:2 ratio were kept at room temperature in an ampoule. The purple colour of the radical was discharged almost immediately, indicating the completion of reaction. After 2 hours, a white solid was deposited. Vacuum fractionation gave the following fractions:-

- (i) an intractable, non-sublimable white solid (0.128 g.) was left behind in the reaction vessel. Its infrared spectrum contains one broad band at 1125 cm^{-1} (due to a trifluoromethyl group attached to antimony) and another band of moderate intensity at 665 cm^{-1} . It did not react with anhydrous hydrogen chloride, but was hydrolysed by 20% sodium hydroxide solution at room temperature to give fluoroform;
- (ii) a colourless liquid (0.178 g.) was obtained in the -40°C trap. The vapour infrared spectrum shows bands characteristic of the $(\text{CF}_3)_2\text{NO}$ and CF_3 groups: 1885w, 1808s, 1466w, 1370s, 1325vs, 1280vs, 1240vs, 1190vs, 1145vs, sh, 1125vs, 1095vs, 1070s, 970s, 800m, 710s, cm^{-1} . It decomposed rapidly to a white solid on standing at room temperature;

- (iii) another colourless liquid (0.134 g.) was found in the -65°C trap which had an infrared spectrum identical to that of (ii);
- (iv) tris(trifluoromethyl)hydroxylamine (0.274 g., 1.16 mmoles), was confirmed by its infrared spectrum and molecular weight; and
- (v) the fraction trapped at liquid air temperature consisted of a mixture of products (0.073 g.). Trifluoromethylisocyanate, perfluoro-2-azapropene and silicon tetrafluoride were believed to be present from the infrared spectrum recorded: 2310s, 2370s (doublet), 1960m, 1930m (doublet), 1805vs, 1460s, 1460s, 1328s, 1300s, 1205vs, 1160sh, 1155s, 1030s, 1010sh, 1000s, 775m, 725m, 710w cm^{-1} .

In another experiment, a mixture of tris(trifluoromethyl)stibine (0.755 g., 2.30 mmoles) and bis(trifluoromethyl)nitroxyl (0.769 g., 4.58 mmoles) was allowed to react at -74°C . The purple colour was completely discharged within 1 hour. As the stibine derivative was unstable at room temperature, the products were not vacuum fractionated in the conventional way, but the following method of separation was adopted instead.

Tris(trifluoromethyl)hydroxylamine (0.497 g., 2.10 mmoles) was distilled off from the reaction vessel which was maintained at -30°C into a liquid air trap, passing -60°C and -84°C traps. Nothing was trapped at -60°C and -84°C traps. The stibine derivative, which remained behind at -30°C , was immediately analysed by hydrolysis with 20% sodium hydroxide solution, giving a quantitative yield of fluoroform. The infrared spectrum of this stibine derivative is similar to those recorded for fractions (ii) and (iii) from the previous reaction.

Hydrolysis of $(\text{CF}_3)_2\text{NOSb}(\text{CF}_3)_2$

About 25 ml of 20% sodium hydroxide solution were added to the above quantity of stibine derivative which was initially chilled at -74°C . The reaction vessel containing the mixture was then removed from the saturated acetone-dry-ice bath and left at room temperature. Hydrolysis proceeded smoothly to give a quantitative yield of fluoroform (0.305 g., 4.36 mmoles; 97.3% yield based on the amount of $(\text{CF}_3)_3\text{Sb}$ used) in 24 hours.

The result clearly indicated that two equivalent moles of fluoroform were eliminated from [bis(trifluoromethyl)nitroxyl]bis(trifluoromethyl)-stibine.

Reaction of $(CF_3)_2NOSb(CF_3)_2$ with anhydrous hydrogen chloride

Excess anhydrous hydrogen chloride was reacted with $(CF_3)_2NOSb(CF_3)_2$ which yielded crude bis(trifluoromethyl)chlorostibine ($-40^\circ C$ and $-60^\circ C$ traps), and bis(trifluoromethyl)hydroxylamine ($-84^\circ C$ trap) (0.272 g., 1.61 mmoles; 96.4% yield based on the quantity of tris(trifluoromethyl)-stibine reacted). Tris(trifluoromethyl)stibine ($-126^\circ C$ trap and excess hydrogen chloride ($-196^\circ C$ trap) were also detected. Attempts to purify the crude compound were unsuccessful since it disproportionated rapidly to tris(trifluoromethyl)stibine and antimony trichloride at room temperature [27].

(b) With four moles of bis(trifluoromethyl)nitroxyl

The reaction of tris(trifluoromethyl)stibine (0.351 g., 1.07 mmoles) with bis(trifluoromethyl)nitroxyl (0.726 g., 4.32 mmoles) produced a white solid after 24 hours of standing at -65° . Vacuum fractionation yielded (i) liquids trapped at $-40^\circ C$ (0.103 g.) and $-70^\circ C$ (0.052 g.), both fractions containing $(CF_3)_2NO$ and CF_3 groups as indicated by their infrared spectra, (ii) tris(trifluoromethyl)hydroxylamine (0.477 g.) trapped at $-126^\circ C$, and (iii) a mixture of trifluoromethylisocyanate, perfluoro-2-azapropene and silicon tetrafluoride (0.130 g.) trapped at liquid air temperature. A white solid remained behind in the reaction vessel. It did not react with anhydrous hydrogen chloride, but interacted vigorously with 20% sodium hydroxide solution to liberate fluoroform on heating. The liquids at $-40^\circ C$ and $-70^\circ C$ decomposed to give white solids on warming to room temperature. The infrared spectrum of the $-40^\circ C$ fraction gave the following peaks: 1850s, 1780m, 1640s, 1450s, 1320vs, 1270vs, 1230vs, 1170vs, 1155vs, 1120m, 1095s, 1060vs, 975vs, 950w, 910w, 810w, 715s cm^{-1} , and the $-70^\circ C$ fraction gave peaks located at 1890w, 1790vs, 1305vs, 1280vs, 1232vs, 1215s, 1198s, 1160sh, 1070s, 990sh, 970vs, 800w, 715w, 715vs, 675m cm^{-1} . Peaks of the liquid air fraction consisted of 2308w, 2272s, 2180m, 1808s, 1460s, 1328s, 1300s, 1280vs, 1245vw, 1205vs, 1185w, 1163sh, 1155s, 1030vs, 1010s, 1000s, 775m, 725m, 710m cm^{-1} .

(c) With six moles of bis(trifluoromethyl)nitroxyl

A mixture of tris(trifluoromethyl)stibine (0.400 g., 1.22 mmoles) and bis(trifluoromethyl)nitroxyl (1.20 g., 7.14 mmoles) was set aside to react at -70°C . On standing overnight at this temperature, a white amorphous solid was obtained. However the purple colour of the nitroxyl radical was not completely discharged. Trap-to-trap fractional condensation in vacuo gave (i) liquids at -40°C (0.122 g.) and -70°C (0.109 g.) which were shown by their infrared spectra to contain $(\text{CF}_3)_2\text{NO}$ and CF_3 groups, (ii) a mixture of tris(trifluoromethyl)hydroxylamine and bis(trifluoromethyl)nitroxyl (0.685 g.) at -126°C , and (iii) a mixture of trifluoromethylisocyanate, perfluoro-2-azapropene and silicon tetrafluoride (0.152 g.) at liquid air temperature. A white solid remained in the reaction vessel. It was inert towards anhydrous hydrogen chloride, but interacted with 20% sodium hydroxide solution to give fluoroform. The infrared spectra (vapour) of the -40°C fraction gave the following bands: 1352s, 1785vs, 1320vs, 1280vs, 1225vs, 1195m, 1126m, 1093w, 1065s, 1006w, 975s, 800m, 770w, 715s, 685w cm^{-1} . The -70°C fraction gave peaks at 1920w, 1893s, 1856w, 1795vs, 1320vs, 1280vs, 1225vs, 1180s, 1140vs, 1065s, 1043s, 997s, 973vs, 805m, 715vs, 685m cm^{-1} . Bands at the liquid air fraction are located at: 2307w, 2275s, 2180s, 1805s, 1462s, 1325s, 1300s, 1280vs, 1245s, 1207vs, 1165s, 1155s, 1028vs, 1011s, 1002s, 773s, 727m, 712m, 630s cm^{-1} .

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REFERENCES

- 1 S.P. Makarov, M.A. Englin, A.F. Videiko, V.A. Tobolin and S.S. Dubov, Dokl. Akad. Nauk SSSR, 168(2), 344 (1966).
- 2 C.S.C. Wang and J.M. Shreeve, Inorg. Chem., 12, 81 (1973).
- 3 H.G. Ang and K.F. Ho, submitted to J. Fluorine Chem.
- 4 H.G. Ang, Chem. Commun., 1320 (1968).

- 5 H.G. Ang and K.F. Ho, *J. Organometal. Chem.*, 19, P19 (1969).
- 6 H.G. Ang and K.F. Ho, *J. Organometal. Chem.*, 27, 349 (1971).
- 7 Y.O. El Nigumi and H.J. Emeleus, *J. Inorg. Nucl. Chem.*, 32, 3213 (1970).
- 8 D.A. Barr and R.N. Haszeldine, *J. Chem. Soc.*, 1881 (1955).
- 9 D.A. Barr and R.N. Haszeldine, *J. Chem. Soc.*, 3428 (1956).
- 10 J.W. Dale, H.J. Emeleus, R.N. Haszeldine and J.H. Moss, *J. Chem. Soc.*, 3708 (1957).
- 11 C.N. Chremcs and R.A. Zingaro, *J. Organometal. Chem.*, 22, 637 (1970).
- 12 G.G. Long, G.C. Doak and L.D. Freedman, *J. Amer. Chem. Soc.*, 85, 209 (1964).
- 13 M. Shindo and R. Okawaro, *J. Organometal. Chem.*, 5, 537 (1966).
- 14 G.H. Bridges and W.E. McEwen, *Tetrahedron Lett.*, 5299 (1966).
- 15 H.J. Emeleus, J.M. Shreeve and P.M. Spaziante, *J. Chem. Soc. (A)*, 3, 431 (1969).
- 16 R.N. Haszeldine and B.O. West, *J. Chem. Soc.*, 3631 (1956).
- 17 R.N. Haszeldine and B.O. West, *J. Chem. Soc.*, 3880 (1957).
- 18 H.G. Ang and H.J. Emeleus, *J. Chem. Soc. (A)*, 1334 (1968).
- 19 F.W. Bennett, H.J. Emeleus and R.N. Haszeldine, *J. Chem. Soc.*, 1565 (1953).
- 20 H.G. Ang, J.S. Coombes and V. Sukhoverkhov, *J. Inorg. Nucl. Chem.*, 31, 877 (1969).
- 21 H.J. Emeleus, J.M. Shreeve and P.M. Spaziante, *Chem. Commun.*, 1253 (1968).
- 22 J. Mason, *J. Chem. Soc.*, 4531 (1963).
- 23 W.D. Blackley and R.R. Reinhard, *J. Amer. Chem. Soc.*, 87, 802 (1965).
- 24 D.P. Babb and J.M. Shreeve, *Inorg. Chem.*, 6, 351 (1967).
- 25 G.G. Flaskerud and J.M. Shreeve, *Inorg. Chem.*, 8, 2065 (1969).
- 26 J.A. Young, S.N. Tsoukalas and R.D. Dresdner, *J. Amer. Chem. Soc.*, 82, 396 (1960).
- 27 J.W. Dale, H.J. Emeleus, R.N. Haszeldine and J.F. Moss, *J. Chem. Soc.*, 3708 (1957).