Journal of Fluorine Chemistry, 27 (1985) 433–450

Received: July 31, 1984; accepted: January 7, 1985

REACTIONS OF BIS(TRIFLUOROMETHYL)NITROXYL WITH $(CF_3)_2AsX$ (WHERE X = F, Cl and Br)

H. G. ANG AND K. K. SO

Chemistry Department, National University of Singapore, Kent Ridge,
Singapore 0511 (Republic of Singapore)

SUMMARY

$(CF_3)_2AsX$ (X = F, Cl) give at elevated temperatures substitution reactions with $(CF_3)_2NO$ to afford $(CF_3)_2NOAs(CF_3)X$ and $(CF_3)_2NOCF_3$. The formation of addition products at low temperatures to give $[(CF_3)_2NO]_2As(CF_3)_2X$, followed by elimination reactions at elevated temperatures to give the final products provide for the first time direct evidence for the mechanisms of the substitution reactions. With $(CF_3)_2AsBr$, bromine was initially displaced to afford $(CF_3)_2NOAs(CF_3)_2$, followed by addition reactions to give $[(CF_3)_2NO]_3As(CF_3)_2$.

INTRODUCTION

The reactions of bis(trifluoromethyl)nitroxyl with trifluoromethyl-substituted derivatives of arsenic follow several courses. The nitroxyl has been found to give (a) substitution reactions with $(CF_3)_3As$ [1], (b) addition reactions with tris(pentafluorophenyl)arsine and $(CH_3)_{3-n}As(CF_3)_n$ (where n = 0, 1, or 2) [2, 3], and (c) halogen displacement reactions with $(CF_3)_2AsI$ [4, 5]. This paper presents results obtained from further investigations between the nitroxyl and $(CF_3)_2AsX$ (X = F, Cl, Br).

0022-1139/85/$3.30

RESULTS AND DISCUSSION

A 2:1 ratio of bis(trifluoromethyl)nitroxyl and bis(trifluoromethyl)fluoroarsine reacted smoothly at -83°C to give the pentavalent arsenic derivative, $[(CF_3)_2NO]_2(CF_3)_2AsF$, in 93% yield, as shown by the equation:

$$(CF_3)_2AsF + 2(CF_3)_2NO \longrightarrow [(CF_3)_2NO]_2As(CF_3)_2F \quad (I)$$

Compound (I) is very sensitive to moisture to afford N,N-bis(trifluoromethyl)hydroxylamine. Alkaline hydrolysis with 20% aqueous sodium hydroxide gives an almost quantitative yield of trifluoromethane (98%). On reacting with anhydrous hydrogen chloride at room temperature for 2 days, it gave a quantitative yield of N,N-bis(trifluoromethyl)hydroxylamine together with a 53% yield of bis(trifluoromethyl)arsenic trichloride. Silicon tetrafluoride was also found at the liquid air trap, together with excess anhydrous hydrogen chloride.

Hence the reaction of compound (I) with anhydrous hydrogen chloride can be represented as follows:

$$[(CF_3)_2NO]_2As(CF_3)_2F + 2HCl \longrightarrow (CF_3)_2AsFCl_2 + 2(CF_3)_2NOH$$

The formation of bis(trifluoromethyl)arsenic trichloride, $(CF_3)_2AsCl_3$, is probably due to the disproportionation of $(CF_3)_2AsFCl_2$ as shown below:

$$3(CF_3)_2AsFCl_2 \longrightarrow 2(CF_3)_2AsCl_3 + (CF_3)_2AsF_3$$

The presence of silicon tetrafluoride could have arisen from the fluorination of the glass ampoule by $(CF_3)_2AsF_3$.

Compound (I) is stable at room temperature. When heated to 70°C for four days, it underwent decomposition to afford tris(trifluoromethyl)hydroxylamine and a colourless liquid of bis(trifluoromethyl)-

nitroxy(trifluoromethyl)fluoroarsine, $(CF_3)_2NOAs(CF_3)F$ (II), as shown by the equation:

$$[(CF_3)_2NO]_2As(CF_3)_2F \longrightarrow (CF_3)_2NOAs(CF_3)F + (CF_3)_2NOCF_3 \qquad (1)$$

Compound (II) reacted with anhydrous hydrogen chloride to give a quantitative yield of N,N-bis(trifluoromethyl)hydroxylamine.

Bis(trifluoromethyl)nitroxyl reacted with bis(trifluoromethyl)-chloroarsine in a similar way at low temperatures to form an oxidative addition product, bis(trifluoromethyl)chloroarsenic di[bis(trifluoromethyl)-nitroxide] (III), in 92% yield.

$$(CF_3)_2AsCl + 2(CF_3)_2NO \longrightarrow [(CF_3)_2NO]_2As(CF_3)_2Cl$$

On standing for 3 days, compound (III) liberated tris(trifluoromethyl)hydroxylamine. Compound (III) is also sensitive to moisture, in which it was hydrolysed to afford N,N-bis(trifluoromethyl)hydroxylamine.

Complete elimination reactions of compound (III) occurred when it was heated at 75°C for 4 days in a sealed ampoule to give an equimolar quantity of tris(trifluoromethyl)hydroxylamine. The second major product was bis(trifluoromethyl)chloroarsine, obtained in 51% yield. The rest were tri[bis(trifluoromethyl)nitroxy]arsine (13%), trifluoromethyl-dichloroarsine and a small amount of a liquid believed to be bis(trifluoromethyl)nitroxytrifluoromethylchloroarsine. Thus the overall reactions can be represented by the following equation:

$$[(CF_3)_2NO]_2As(CF_3)_2Cl \longrightarrow (CF_3)_2NOAs(CF_3)Cl + (CF_3)_2NOCF_3 \qquad (2)$$

The formations of $[(CF_3)_2NO]_3As$, $(CF_3)_2AsCl$ and CF_3AsCl_2 most probably arise from the disproportionation of $(CF_3)_2NOAs(CF_3)Cl$, as shown by the equation:

$$3(CF_3)_2NOAs(CF_3)Cl \longrightarrow [(CF_3)_2NO]_3As + CF_3AsCl_2 + (CF_3)_2AsCl \qquad (3)$$

A mixture of bis(trifluoromethyl)bromoarsine and bis(trifluoromethyl)nitroxyl was allowed to react in a temperature bath at -78°C. At the end of 20 hours, the temperature had risen to 10°C. Orange bromine vapour appeared.

On fractionation of the products, 42% of bromine was obtained. A fraction, trapped at -78°C as a white solid (passed the -45°C trap), was identified from its infrared spectrum and elemental analysis to be bis(trifluoromethyl)nitroxy(trifluoromethyl)arsine, $(CF_3)_2NOAs(CF_3)_2$. The yield was 26%. The infrared spectrum was identical to that of an authentic sample prepared before by reacting tris(trifluoromethyl)arsine with bis(trifluoromethyl)nitroxyl at room temperature [4]:

$$(CF_3)_3As + 2(CF_3)_2NO \longrightarrow (CF_3)_2AsON(CF_3)_2 + (CF_3)_2NOCF_3$$

The major fraction from the reaction of bis(trifluoromethyl)bromoarsine with bis(trifluoromethyl)nitroxyl was a mixture of colourless liquid and white crystalline solid trapped at -45°C (passed the -10°C trap). If this fraction were left undisturbed, more white crystalline solid would appear at the bottom of the trap. Once the trap was disturbed or was shaken briskly, the solids began to dissolve again. When the mixture was kept overnight at room temperature, it became a homogeneous colourless liquid.

The two components could not be separated by conventional vacuum fractionation. Complete separation of these two components was achieved according to the method of Ang and Lien [6]. The separation technique takes advantage of the small difference in the melting points of both compounds.

The infrared spectra of both compounds in the vapour phase are identical. They indicate the presence of two trifluoromethyl groups bonded to the arsenic atom as well as the presence of bis(trifluoromethyl)nitroxyl group, whose peaks appear at 1105 - 1185 and 1205 - 1320 cm^{-1}, respectively. For trivalent bis(trifluoromethyl)nitroxy-arsenic compounds, the N-O stretching vibrations are observed in the region 1025-1030 cm^{-1}. For pentavalent arsenic derivatives, the N-O stretching frequencies are observed at higher frequencies, as shown in Table 1.

TABLE 1

The N-O stretching vibration of bis(trifluoromethyl)nitroxyarsenic (V) compounds

Compound	N-O stretching (cm^{-1})	Reference
$Me_3As[ON(CF_3)_2]_2$	1058	6
$Me_2(CF_3)As[ON(CF_3)_2]_2$	1060	6
$Me(CF_3)_2As[ON(CF_3)_2]_2$	1056	6
$Cl(CF_3)_2As[ON(CF_3)_2]_2$	1040	-
$F(CF_3)_2As[ON(CF_3)_2]_2$	1040	-
$(C_6F_5)_3As[ON(CF_3)_2]_2$	1030	7

The above evidence strongly suggests that the solid and liquid compounds are isomers of the penta-arsenic derivative $(CF_3)_2As[ON(CF_3)_2]_3$, the formation of which can be represented by the equation:

$$2(CF_3)_2AsBr + 4(CF_3)_2NO \longrightarrow (CF_3)_2As[ON(CF_3)_2]_3\ (52\%) + Br_2 + (CF_3)_2AsON(CF_3)_2\ (26\%)$$

The pentavalent arsenic derivative is hydrolysed by moisture to yield N,N-bis(trifluoromethyl)hydroxylamine. The isomers are not volatile enough for their vapour pressures to be measured.

OBSERVATIONS

Bis(trifluoromethyl)nitroxyl reacts with $(CF_3)_2AsX$ (where X = F, Cl) to give addition products. Both the pentavalent arsenic compounds, $[(CF_3)_2NO]_2As(CF_3)_2X$ (where X = F and Cl), undergo elimination reactions on heating, according to equations (1) and (2).

The fluoro-derivative, isolated as one of the products, is stable whereas the chloro-derivative, $(CF_3)_2NOAs(CF_3)Cl$, is unstable at elevated temperatures and undergoes disproportionation according to equation (3).

Both the addition reactions followed by the elimination reactions of the pentavalent arsenic compounds provide for the first time direct evidence for the substitution reactions occurring between bis(trifluoromethyl)nitroxyl and $(CF_3)_2AsX$ (X = F, Cl) at elevated temperatures. These findings give support for similar mechanisms that have been proposed earlier for the stepwise substitution reactions between $(CF_3)_3As$ and $(CF_3)_2NO$ wherein $[(CF_3)_2NO]_nAs(CF_3)_{3-n}$ (n = 1, 2, 3) and $(CF_3)_2NOCF_3$ were obtained [1, 2].

The reactions of bis(trifluoromethyl)nitroxyl with bis(trifluoromethyl)bromoarsine follow a different course involving the displacement of bromine to give both the trivalent and pentavalent arsenic derivatives as shown by the following free radical sequence:

$$(CF_3)_2NO + (CF_3)_2AsBr \longrightarrow (CF_3)_2NOAs(CF_3)_2 + \frac{1}{2}Br_2$$

$$(CF_3)_2NOAs(CF_3)_2 + (CF_3)_2NO \longrightarrow [(CF_3)_2NO]_2As(CF_3)_2$$

$$[(CF_3)_2NO]_2As(CF_3)_2 + (CF_3)_2NO \longrightarrow [(CF_3)_2NO]_3As(CF_3)_2$$

The hydrolysis reactions and the reactions of hydrogen chloride with arsenic compounds are diagnostic of trifluoromethyl and bis(trifluoromethyl)nitroxy groups bonded to arsenic respectively. The results are summarised in Tables 2 and 3.

EXPERIMENTAL

Infrared spectra were determined with a Perkin Elmer 337 Grating Infrared Spectrophotometer which covers the range 4000-400 cm^{-1}. $(CF_3)_2AsX$ (X = F, Cl, Br, CN) were prepared by reacting the iodo analogue with the mercuric salts [8].

Reaction of bis(trifluoromethyl)fluoroarsine with bis(trifluoromethyl)nitroxyl

Bis(trifluoromethyl)fluoroarsine (0.5526 g, 2.38 mmoles) was condensed *in vacuo* with bis(trifluoromethyl)nitroxyl (0.8100 g, 4.82 mmoles) into a glass ampoule of 70 ml capacity. The ampoule was placed in the ethyl acetate slush (-83°C) and warmed up slowly to room temperature. The next day, a slightly blue heavy liquid remained in the ampoule.

TABLE 2

Hydrolysis by 20% sodium hydroxide

Compound	(g. mmole)	Temp.(°C)/hr	CF_3H: g. mmole	Percent Yield
$R_2(CF_3)_2AsF$	0.149, 0.26	150/72	0.0355, 0.51	98
$R_2(CF_3)_2AsCl$	0.148, 0.25	120/96	0.0279, 0.40	80
$(CF_3)_2AsCl_3$	0.100, 0.31	120/96	0.032, 0.46	74

R = $(CF_3)_2NO$

TABLE 3

Reactions of bis(trifluoromethyl)nitroxy derivatives with hydrogen chloride

Reactants	(g. mmole)	Temp.(°C)/hr	$(CF_3)_2NOH$ (g., mmole)	Percent Yield
$R_2(CF_3)_2AsF$	0.430, 0.76	28/48	0.258, 1.58	104
$R_2(CF_3)_2AsCl$	0.235, 0.40	28/96	0.143, 0.84	105
$R_3As(CF_3)_2$ solid	0.151, 0.21	28/48	0.106, 0.62	98
$R_3As(CF_3)_2$ liquid	0.116, 0.16	28/48	0.086, 0.50	104

R = $(CF_3)_2NO$

Fractionation of the product mixture yielded two fractions:

(i) A colourless liquid, trapped at -50°C (passed the -10°C trap), was identified as bis(trifluoromethyl)fluoroarsenic di[bis(trifluoromethyl)nitroxide](I) (nc) (1.2622 g, 2.22 mmoles; yield 93%) based on the amount of the arsine used). The infrared absorption bands of compound (I) were located at 1315vs, 1270vs, 1235vs, 1220sh, 1200s, 1155m, 1110m, 1040m, 971m, 802m, 745m, 710m, 675m and 580w cm^{-1}.

(ii) Excess bis(trifluoromethyl)nitroxyl (0.047 g, 0.28 mmole) was recovered at the -196°C trap (passed the -78°C trap).

Hydrolysis of bis(trifluoromethyl)fluoroarseni cdi[bis(trifluoromethyl)nitroxide] with 20% aqueous sodium hydroxide

Bis(trifluoromethyl)fluoroarsenic di[bis(trifluoromethyl)nitroxide] (0.1487 g, 0.26 mmole) was sealed into a glass ampoule containing 5 ml of 20% aqueous sodium hydroxide. The ampoule was heated at 150°C for 3 days.

On fractionation, the only volatile fraction gave 0.0355 g (0.51 mmole) of trifluoromethane (Found: mol. wt. 70; CF_3H requires mol. wt. 70), giving a yield of 98%.

Reaction of bis(trifluoromethyl)fluoroarsenic di[bis(trifluoromethyl)-nitroxide] with excess anhydrous hydrogen chloride

Bis(trifluoromethyl)fluoroarsenic di[bis(trifluoromethyl)nitroxide] (0.4304 g, 0.76 mmole) was condensed in vacuo with excess anhydrous hydrogen chloride (0.1448 g, 3.97 mmoles) into a glass ampoule, and then left to stand at room temperature for two days.

Fractionation of the mixture yielded three fractions:

(i) a white solid trapped at the -65°C trap (passed the -40°C trap) was found to be bis(trifluoromethyl)arsenic trichloride, (0.1280 g, 0.40 mmole, 53% yield; found: Cl, 34.8%, $C_2Cl_3F_6As$ requires Cl, 33.3%). The infrared spectrum identical to that of an authentic sample.

Bis(trifluoromethyl)arsenic trichloride (0.1280 g, 0.40 mmole), when hydrolysed by 5 ml of 20% aqueous sodium hydroxide, afforded trifluoromethane (0.0530 g, 0.76 mmole) in 95% yield;

(ii) a quantitative yield of N,N-bis(trifluoromethyl)hydroxylamine (0.2578 g, 1.58 mmoles) at the -95°C trap (passed the -65°C trap); and

(iii) excess hydrogen chloride and a small amount of silicon tetrafluoride was trapped at the -196°C trap.

Pyrolysis of bis(trifluoromethyl)fluoroarsenic di-[bis(trifluoromethyl)nitroxide]

Bis(trifluoromethyl)fluoroarsenic di[bis(trifluoromethyl)nitroxide] (0.4706 g, 0.83 mmole) was sealed in vacuo into a 80 ml glass ampoule.

The ampoule was heated at 70°C for four days.

Fractionation of the products gave three fractions:

(i) the starting arsenic compound (0.2219 g, 0.39 mmole, 47% recovery), trapped at the -78°C trap (passed the -30°C trap) and confirmed by its infrared spectrum.

Hydrolysis of the colourless liquid (0.1022 g, 0.18 mmole) by 5 ml of 20% aqueous sodium hydroxide at 130°C for 2 days gave trifluoromethane (0.252 g, 0.36 mmoles, yield 100%; mol. wt., 70; CF_3H requires mol. wt. 70);

(ii) bis(trifluoromethyl)nitroxy(trifluoromethyl)fluoroarsine (II) (0.1012 g, 0.31 mmole) was trapped at -30°C. The major infrared absorptions were located at 1310vs, 1279vs, 1232vs, 1220vs, 1190sh, 1145vs, 1110m, 1028s, 971s, 800m, 745w, 710s, 700sh, 675w and 575w cm^{-1}.

Compound (II) (0.1012 g, 0.31 mmole) reacted with anhydrous hydrogen chloride to yield and equimolar quantity of N,N-bis(trifluoromethyl)hydroxylamine (0.0510 g, 0.30 mmoles); and

(iii) a white solid in the -196°C trap was identified by its infrared spectrum to be tris(trifluoromethyl)hydroxylamine (0.0931 g, 0.39 mmole; found: mol. wt. 238, C_3F_9NO requires mol. wt. 237). The infrared spectrum gave peaks at 1360w, 1321vs, 1290vs, 1248vs, 1210m, 1185vs, 1065m, 970m, 715m and 685w cm^{-1}.

Reaction of bis(trifluoromethyl)chloroarsine with bis(trifluoromethyl)nitroxyl

Bis(trifluoromethyl)chloroarsine (0.4133 g, 1.66 mmoles) and bis(trifluoromethyl)nitroxyl (0.5576 g, 3.32 mmoles) were condensed *in vacuo* into a Pyrex ampoule of 50 ml capacity. It was then sealed and allowed to warm up from -95°C in a toluene slush over night to 10°C. The colour of the radical was almost completely discharged. A heavy colourless liquid together with a small amount of solid iodine were formed. The formation of iodine was probably due to the presence of a small amount of bis(trifluoromethyl)iodoarsine, from which the bis(trifluoromethyl)chloroarsine was previously prepared.

Fractionation of the product mixture yielded two main fractions:

(i) a colourless liquid, trapped at -25°C (passed the -15°C trap slowly), was found to be bis(trifluoromethyl)chloroarsenic di[bis(trifluoromethyl)nitroxide] (III) (nc) (0.7407 g, 1.27 mmoles; the yield was 76.4%) and elemental analysis: Cl, 6.3%, $C_3F_{18}Cl_2O_2As$ requires Cl, 6.1%);

(ii) a mixture of unreacted bis(trifluoromethyl)chloroarsine and bis(trifluoromethyl)nitroxyl (0.0345 g) was recovered at the -196°C trap (passed the -78°C trap);

In a second reaction, the bis(trifluoromethyl)chloroarsine had been treated with mercury to remove the last trace of bis(trifluoromethyl)iodoarsine before reacting with the nitroxyl radical (0.5083 g, 3.02 mmoles). The reaction mixture was allowed to warm up to room temperature. On fractionation, it was found that all the bis(trifluoromethyl)chloroarsine (0.3638 g, 1.46 mmoles) had reacted to yield 0.7877 g (1.35 mmoles) of bis(trifluoromethyl)chloroarsenic di[bis(trifluoromethyl)-nitroxide]. Thus the yield was raised to 92%. No iodine was found in the reaction mixture.

The product gave an infrared spectrum with absorptions at 1310vs, 1270vs, 1260vs, 1225vs, 1220sh, 1181vs, 1091m, 1040m, 972m, 805w, 788w,730w, 715m, 580w and 560sh cm^{-1}. The product could be easily hydrolysed in air, liberating N,N-bis(trifluoromethyl)hydroxylamine.

Reaction of bis(trifluoromethyl)chloroarsenic di[bis(trifluoromethyl)-nitroxide] with 20% aqueous sodium hydroxide

Bis(trifluoromethyl)chloroarsenic di[bis(trifluoromethyl)nitroxide] (0.1483 g, 0.25 mmole) was introduced into a glass ampoule containing 7 ml of 20% aqueous sodium hydroxide. The ampoule was heated at 120°C for 4 days. Some white solids appeared in the sodium hydroxide solution. Fractionation of the reaction mixture yielded trifluoromethane (0.0279 g, 0.40 mmole; 80% yield), which was trapped at the -196°C trap (passed the -120°C trap). The remaining solution was used for chloride analysis. (Found: Cl, 6.3%; $C_6F_{18}ClN_2O_2As$ requires Cl, 6.1%).

Reaction of bis(trifluoromethyl)chloroarsenic di[bis(trifluoromethyl)-nitroxide] with excess anhydrous hydrogen chloride

Bis(trifluoromethyl)chloroarsenic di[bis(trifluoromethyl)nitroxide] (0.2350 g, 0.40 mmole) and anhydrous hydrogen chloride (0.0619 g, 1.70 mmoles) were sealed in vacuo into a 30 ml ampoule, which was then left at room temperature for 4 days. A colourless liquid remained in the ampoule.

On fractionation of the reaction mixture, three fractions were obtained:

(i) bis(trifluoromethyl)arsenic trichloride (0.100 g, 0.31 mmole; yield 78%) was trapped as a white solid at the -70°C trap, passed the -30°C trap. It was a colourless oil at room temperature. The major infrared absorptions were located at 1275vw, 1222m, 1205vs, 1168vw, 1130vw, 1095sh, 1080vs (broad), 785vw and 735m cm^{-1};

(ii) N,N-bis(trifluoromethyl)hydroxylamine (0.1431 g, 0.84 mmole) was trapped at the -95°C trap (passed the -70°C trap). Hence two moles of the hydroxylamine was liberated from 1 mole of the compound; and

(iii) excess hydrogen chloride (0.0326 g) was recovered at the -196°C trap.

Hydrolysis of bis(trifluoromethyl)arsenic trichloride by 20% aqueous sodium hydroxide

Bis(trifluoromethyl)arsenic trichloride (0.1000 g, 0.31 mmole) was condensed in vacuo into a 100 ml glass ampoule containing 5 ml 20% aqueous sodium hydroxide. The ampoule was heated to 120°C for four days. Some white solids developed inside the glass ampoule after heating.

On fractionation, the only volatile product was trifluoromethane (0.0320 g, 0.46 mmole; found: mol. wt. 70; CF_3H requires mol. wt. 70; giving a yield of 74%).

The non-volatile fractions were analysed for chloride. The solid was found to be slightly soluble in aqueous sodium hydroxide. On acidification with 5% nitric acid, a small amount of white precipitate was formed. The solution was then filtered before the addition of silver nitrate solution. The weight of silver chloride obtained was 0.1321 g, which gave Cl, 32.6%; $C_2F_6Cl_3As$ requires Cl, 33.2%.

Pyrolysis of bis(trifluoromethyl)chloroarsenic di[bis(trifluoromethyl)nitroxide]

Bis(trifluoromethyl)chloroarsenic di[bis(trifluoromethyl)nitroxide] (0.5477 g, 0.93 mmole) was heated at 75°C for 4 days in a sealed glass ampoule of 50 ml capacity. After heating, the content in the ampoule remained as a colourless liquid. On fractionation, it gave the following fractions:

(i) tri[bis(trifluoromethyl)nitroxy]arsine (0.0722 g, 0.12 mmole; yield 13%). It was trapped at the -30°C trap as colourless, long, needle-shaped crystals. The infrared spectrum was identical to that of an authentic sample. The major absorptions were located at 1305vs, 1290sh, 1268vs, 1232vs, 1228sh, 1210s, 1024s, 970s, 799m, 744m, 710s, 700m and 580m cm^{-1};

(ii) bis(trifluoromethyl)nitroxy(trifluoromethyl)chloroarsine (0.0689 g, 0.19 mmole, yield 20%) was trapped at the -50°C trap (passed the -30°C trap) as a colourless liquid. The major infrared absorptions were located at 1305vs, 1265sh, 1260vs, 1230vs, 1210m, 1185w, 1135m (broad), 1020m, 970m, 795w and 710m cm^{-1}. 0.0689 g (0.19 mmole) of the compound was allowed to react with excess anhydrous hydrogen chloride for two days. N,N-bis(trifluoromethyl)hydroxylamine (0.0319 g, 0.19 mmole) was obtained quantitatively;

(iii) trifluoromethyldichloroarsine (0.0613 g, 0.29 mmoles, yield 31%). It was trapped at -78°C as white crystals (passed the -50°C trap). The infrared spectrum showed a strong and broad absorption at 1130 cm^{-1} (C-F stretching) and a weak absorption at 705 cm^{-1} (CF_3 deformation). (Found: Cl, 32.0%; CCl_2F_3As requires Cl, 33.0%);

(iv) bis(trifluoromethyl)chloroarsine (0.1176 g, 0.47 mmole, yield 51%) was trapped at the -95°C trap (passed the -78°C trap). It was identified by its infrared spectrum; and

(v) tris(trifluoromethyl)hydroxylamine (0.2190 g, 0.92 mmole; yield 99%) trapped at the -126°C trap (passed the -95°C trap). It was identified by its infrared spectrum and molecular weight. (Found: mol. wt. 237; C_3F_9No requires mol. wt. 237.) The infrared spectrum gave peaks at 1360w, 1321vs, 1290vs, 1248vs, 1210m, 1185vs, 1065m, 970m, 715m and 685w cm^{-1}.

Reaction of bis(trifluoromethyl)bromoarsine with bis(trifluoromethyl)nitroxyl

Bis(trifluoromethyl)bromoarsine (0.5690 g, 1.94 mmoles) and bis(trifluoromethyl)nitroxyl (1.0547 g, 6.28 mmoles) were condensed *in vacuo* into a glass ampoule. The sealed ampoule was left in a dry ice/isopropanol mixture (-78°C). After twenty hours, the coolant had warmed up to 10°C. Orange-red vapour together with a colourless liquid developed.

Fractionation of the product mixture yielded three main fractions:

(i) a colourless liquid (called fraction A) trapped at -55°C (1.1662 g). It was a mixture of several compounds;

(ii) bromine (0.1293 g, 0.81 mmole, yield 42%) was trapped as red solids in the -95°C trap (passed the -55°C trap); and

(iii) bis(trifluoromethyl)nitroxyl (0.3176 g, 1.89 mmoles; 30%) was recovered in the -196°C trap (passed the -95°C trap).

On refractionation, fraction A gave the following:

(i) an unidentified, colourless liquid (0.1183 g) trapped at -10°C; the infrared spectrum gave peaks at 1310vs, 1290-1270s(broad), 1250-1230vs(broad), 1210sh, 1180vs, 1130m, 1100m, 1065m, 990m, 970m and 715m cm^{-1}.

(ii) a mixture of colourless liquid and white solids (0.7906 g, 1.10 mmoles; giving a yield of 56.7% based on the amount of bis(trifluoromethyl)bromoarsine used); trapped at the -45°C trap (passed the -10°C trap) identified as a isomeric mixture of bis(trifluoromethyl)arsenic tri[bis(trifluoromethyl)nitroxide]. Attempts made to separate the liquid and solid components by repeated trap-to-trap distillation were not successful. The solid was found to be soluble in the liquid component. If the mixture was allowed to stand longer at room temperature, more solid crystallised out slowly, but on slight shaking of the trap, the crystals dissolved again.

Separation was achieved using the method according to Ang and Lien [6]. Repeated fractionation of 0.7906 g of the isomeric mixture gave 0.3146 g (0.44 mmole; yield of 23%) of the white solid and 0.3988 g (0.56 mmole; yield of 29%) of the colourless liquid. The liquid isomer was not volatile enough for vapour pressure measurements to be made. The infrared spectra of both components were identical, with major absorptions located at 1320vs, 1290vs, 1245vs, 1205vs, 1185vs, 1165sh, 1135s, 1105s, 1068m, 990w, 970m, 800w, 713m and 685 cm^{-1}.

(iii) a white solid (colourless liquid at room temperature), trapped at -78°C (passed -45°C). It was identified as bis(trifluoromethyl)arsenic bis(trifluoromethyl)nitroxide (0.1900 g, 0.50 mmole; yield 26%; found: mol. wt. 384; C, 12.3%; $C_4F_{12}NOAs$ requires mol. wt. 381; C, 12.6%). The infrared spectrum gave peaks located at 1310vs, 1260vs, 1235vs, 1220sh, 1205sh, 1165s, 1145sh, 1130s, 1115sh, 1030m, 970m 798m, 730w, 710m and 575w cm^{-1}, which were identical to those of an authentic sample; and

(iv) a trace amount of the unreacted bis(trifluoromethyl)bromoarsine, trapped at the -196°C trap (passed the -78°C trap).

Reaction of the solid bis(trifluoromethyl)arsenic tri[bis(trifluoromethyl)nitroxide] with anhydrous hydrogen chloride

The solid isomer (0.1507 g, 0.21 mmole) was condensed *in vacuo* with excess anhydrous hydrogen chloride (0.0379 g, 1.04 mmoles) into a glass ampoule. The sealed ampoule was left at room temperature. After 2 days, two colourless immiscible liquids were formed.

Fractionation of the reaction mixture yielded five fractions:

(i) a trace amount of a white solid was trapped at -30°C trap;

(ii) arsenic trichloride (0.0210 g, 0.12 mmole; yield of 55%) was trapped at the -65°C trap as white crystals (passed the -30°C trap). 0.0210 g of the compound was hydrolysed by 3 ml 20% aqueous sodium hydroxide at 90°C for one day. (Analysis: found, Cl, 59.0%; $AsCl_3$ requires Cl, 58.8%);

(iii) bis(trifluoromethyl)hydroxylamine (0.1055 g, 0.62 mmole) was trapped at -83°C (passed the -65°C trap). The yield was 99%. Hence 3 moles of N,N-bis(trifluoromethyl)hydroxylamine were liberated from one mole of arsenic (V) compound;

(iv) bis(trifluoromethyl)chloroarsine (0.0035 g, 0.01 mmole; 7% yield) was trapped at -120°C (passed -83°C); and

(v) a mixture of excess hydrogen chloride and chlorotrifluoromethane (0.0304 g) was trapped at -196°C (passed the -120°C trap). (Found: mol. wt. 51.6; HCl and $CClF_3$ requires mol. wt. 36.5 and 104.5 respectively). The chlorotrifluoromethane could not be separated from hydrogen chloride by refractionation. It is identified by the infrared spectrum which gave a strong absorption at 1210 cm^{-1}, a strong doublet at 1090, 1082 cm^{-1} and a weak triplet at 765, 760 and 750 cm^{-1}.

Reaction of the liquid bis(trifluoromethyl)arsenic tri[bis(trifluoromethyl)nitroxide] with anhydrous hydrogen chloride

The liquid isomer (0.1155 g, 0.16 mmole) was condensed *in vacuo* with excess anhydrous hydrogen chloride (0.0291 g, 0.80 mmole) into a glass ampoule and left to stand at room temperature for 2 days. Two colourless, immiscible liquids resulted.

Vacuum fractionation afforded:

(i) a trace amount of white solid was trapped at the -30°C trap.

(ii) white crystals (colourless gas at room temperature) was trapped at the -50°C trap (passed the -30°C trap). It did not give any infrared absorptions. It was identified as arsenic trichloride (0.0200 g, 0.11 mmole; yield of 69% based on the amount of arsenic(V) compound; found: Cl, 59.8%; $AsCl_3$ requires Cl, 58.5%.);

(iii) bis(trifluoromethyl)chloroarsine was trapped at the -120°C trap (passed the -83°C trap) (0.0070 g, 0.03 mmole; yield of 18% based on the amount of arsenic(V) compound);

(iv) N,N-bis(trifluoromethyl)hydroxylamine (0.0855 g, 0.50 mmoles) was trapped at -83°C (passed -78°C trap). Hence one mole of the arsenic(V) compound yielded 3 moles of N,N-bis(trifluoromethyl)-hydroxylamine; and

(v) a mixture of excess anhydrous hydrogen chloride and chlorotrifluoromethane, was trapped at the -196°C trap (passed the -120°C trap), (0.0249 g; found: mol. wt. 58.5). The infrared spectrum of chlorotrifluoromethane was similar to that obtained in the previous experiment.

REFERENCES

1 H.G. Ang and K.F. Ho, J. Organometal. Chem. 19, (1969) 19; 27, (1971) 349.

2 H.G. Ang and W.S. Lien, J. Fluorine Chem. 3, (1973/74) 235.

3 H.G. Ang and W.S. Lien, J. Fluorine Chem. 9, (1977) 73.

4 H.G. Ang and K.F. Ho, J. Fluorine Chem. 8, (1976) 497.

5 K.K. So, Ph.D. Thesis, National University of Singapore, 1981.

6 H.G. Ang and W.S. Lien, J. Fluorine Chem. 15, (1980) 453.

7 H.G. Ang and Y.C. Syn, J. Fluorine Chem. 8, (1976) 481.

8 E.G. Walaschewski E.G., Chem. Ber. 86, (1953) 272.