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PREPARATION AND PROPERTIES OF BIS(TRIFLUOROMETHYL)-NITROXY DERIVATIVES OF ARSENIC

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SUMMARY

Tris(trifluoromethyl)arsine has been shown to undergo stepwise radical exchange reactions with bis(trifluoromethyl)nitroxide (I) to give $[(CF_3)_2NO]_nAs(CF_3)_{3-n}$ ($n=1,2,3$), and tris(trifluoromethyl)hydroxylamine. [Bis(trifluoromethyl)nitroxy]bis(trifluoromethyl)arsine has also been obtained by treating (I) with bis(trifluoromethyl)arsine, and tris[bis(trifluoromethyl)nitroxy]arsine has been made by treating (I) with elemental arsenic. IR, ^{19}F NMR, and vapour pressure measurements on the new compounds are reported, and some of their reactions are described.

INTRODUCTION

Bis(trifluoromethyl)nitroxide, a stable purple gas at room temperature[1], has been shown to be a good hydrogen abstractor as well as a powerful radical scavenger[2]. Such properties are important, as they have been utilised to advantage in the syntheses of new organic as well as inorganic derivatives[3]. The nitroxide (I) also undergoes addition and metalation reactions [3,4], while with iron at elevated temperatures it is deoxyfluorinated to perfluoro-2-azapropene[2]. We now describe some additional reactions of bis(trifluoromethyl)nitroxide with tris(trifluoromethyl)arsine.

RESULTS AND DISCUSSION

Bis(trifluoromethyl)nitroxide has been found to react smoothly with tris(trifluoromethyl)arsine in a 2/1 molar ratio at ambient temperature. Completion of the reaction is indicated by a gradual discharge of the purple colour. Vacuum fractionation gives two major products, [bis(trifluoromethyl)nitroxy]bis(trifluoromethyl)arsine (II) and tris(trifluoromethyl)hydroxylamine, collected in the −65° and −126° traps, respectively. This result shows that the reaction involves substitution of a trifluoromethyl group by bis(trifluoromethyl)nitroxide according to the eqn.:

$$(CF_3)_3As + 2\,\underset{(I)}{(CF_3)_2NO} \rightarrow \underset{(II)}{(CF_3)_2NOAs(CF_3)_2} + (CF_3)_2NOCF_3$$

The reaction of the nitroxide (I) with bis(trifluoromethyl)arsine provides another convenient route to compound (II), giving almost a 100% yield. The other product is bis(trifluoromethyl)hydroxylamine, and the overall equations are as follows:

$$(CF_3)_2AsH + \underset{(I)}{(CF_3)_2NO} \rightarrow \underset{(A)}{(CF_3)_2As^\bullet} + (CF_3)_2NOH$$

$$(CF_3)_2As^\bullet + \underset{(I)}{(CF_3)_2NO} \rightarrow \underset{(II)}{(CF_3)_2NOAs(CF_3)_2}$$

These reactions indicate that the rate of scavenging of the bis(trifluoromethyl)arsine radical (A) by the nitroxide is much faster than the rate of coupling of bis(trifluoromethyl)arsine radicals.

Tris(trifluoromethyl)hydroxylamine, a stable colourless liquid, was identified by its mol.wt., and its IR spectrum agrees with that reported by Haszeldine and coworkers who prepared it by irradiating a mixture of the nitroxide (I) and trifluoromethyl iodide with UV light.

A series of reactions of tris(trifluoromethyl)arsine with the nitroxide (I) have established that further stepwise substitution reactions lead to novel bis- and tris[bis(trifluoromethyl)nitroxy]arsenic derivatives, and the overall reactions are represented by the following eqns.:

$$\begin{tikzcd}
 & (CF_3)_2NOAs(CF_3)_2 + (CF_3)_2NOCF_3 \arrow[d, "\text{r.t.}"', "+(CF_3)_2NO"] \\
(CF_3)_2NO + (CF_3)_3As \arrow[ur, "\text{r.t.}", "(2/1)"'] \arrow[r, "\text{r.t.}", "(4/1)"'] \arrow[dr, "70^\circ", "6/1"'] & {[(CF_3)_2NO]_2AsCF_3} \quad (III) \arrow[d, "70^\circ"', "+(CF_3)_2NO"] \\
 & {[(CF_3)_2NO]_3As} \quad (IV)
\end{tikzcd}$$

(r.t. = room temperature)

Tris[bis(trifluoromethyl)nitroxy]arsine (IV) can also be prepared in 76% yield, by the reaction of the nitroxide (I) with arsenic metal.

Separation of compounds (III) and (IV) from tris(trifluoromethyl)hydroxylamine presents relatively little difficulty since the latter is fairly volatile, and the bis(trifluoromethyl)nitroxy derivatives of arsenic are trapped at −40° and −20° respectively.

The mono- and bis[bis(trifluoromethyl)nitroxy] derivatives are liquid at room temperature, while compound (IV) melts at 29.5°. They are all susceptible to attack by moisture. Hydrolysis of compounds (II) and (III) by 20% sodium hydroxide at 110° cleaves the CF_3–As bond to give a quantitative yield of trifluoromethane which provides additional confirmation of the composition of the compounds.

Tris[bis(trifluoromethyl)nitroxy]arsine reacts with one mole of hydrogen chloride to afford an almost quantitative yield of $[(CF_3)_2NO]_2AsCl$ and bis(trifluoromethyl)hydroxylamine. With three moles of hydrogen chloride, all the As–O bonds are cleaved to give arsenic trichloride:

$$[(CF_3)_2NO]_3As \begin{cases} \xrightarrow{+HCl} [(CF_3)_2NO]_2AsCl + (CF_3)_2NOH \\ \xrightarrow{+3\,HCl} AsCl_3 + 3\,(CF_3)_2NOH \end{cases}$$

Spectroscopic Studies

The IR absorptions of bis(trifluoromethyl)nitroxy derivatives of arsenic as shown in Table 1 reveal the presence of numerous intense bands from about 1100 to 1350 cm^{-1}, and these absorptions are generally ascribed to the C–F stretching frequencies. The bands appearing in the higher region, generally from 1230–1350 cm^{-1}, are due to the C–F stretching absorptions of bis(trifluoromethyl)nitroxy group(s), and these bands are present in all the compounds listed in Table 1. The frequencies in the lower region, *i.e.* from about 1100 to 1250 cm^{-1}, are ascribed to the C–F stretching vibrations of trifluoromethyl substituents bonded directly to arsenic. That accounts for the presence of more intense bands in $(CF_3)_2AsON(CF_3)_2$ which contains two CF_3(As) groups, and less intense band in $CF_3As[ON(CF_3)_2]_2$ which contains only one CF_3(As) group, together with the absence of such bands in this lower region for the other two bis(trifluoromethyl)nitroxy derivatives of arsenic, this simple pattern is a useful tool for determining whether a new bis(trifluoromethyl)-nitroxy derivative of arsenic compounds has been produced. A new absorption of medium intensity which appears at about 800 cm^{-1} could be tentatively assigned as

TABLE 1

IR SPECTRA OF BIS(TRIFLUOROMETHYL)NITROXY DERIVATIVES OF ARSENIC
R = $(CF_3)_2NO$, frequencies in cm^{-1}.

$(CF_3)_2AsR$	CF_3AsR_2	R_3As	R_2AsCl	Tentative assignment
			1390 w	C–F stretch
1305 s	1325 s	1306 s	1320 s	
1257 vs	1290 vs	1268 vs		
1230 vs	1250 s	1236 vs	1260 vs	
1210 vs	1215 (sh), s	1226 vs	1225 vs	
1198 vs	1185 s			
1160 vs				
1150 vs				
1128 vs	1130 vs			
1110 vs	1105 vw			
	1080 m			
1028 s	1025 m	1026 s	1026 s	N–O stretch
908 s	975 m	970 s	975 s	Symmetric C–N–C stretch
798 m		880 m	800 m	As–O stretch
740 (sh), w		747 m		C–N–C bending
730 w				C–F deformation
	717 m	711 m	715 m	
	690 w			
578 w		583 m		
		553 w		
		400 w		

the As–O stretching vibration. The peak at about 710 cm^{-1} can be attributed to the C–F deformation mode.

^{19}F NMR spectrum of [bis(trifluoromethyl)nitroxy]bis(trifluoromethyl)arsine consists of two peaks of similar intensity; the chemical shifts are $\varphi[(CF_3)_2As] = 63.0$ ppm and $\varphi[(CF_3)_2NO] = 76.4$ ppm. Appreciable F(CN)–F(CAs) coupling (1.4 Hz) causes splitting of each peak into a 1/6/15/20/15/6/1 septet, which is of interest because the fluorine atoms are separated by five atoms.

Discussion of substitution reactions

Thus far, tris(trifluoromethyl)arsine has been shown to undergo exchange reactions with both methyl iodide and *N*-halogenobis(trifluoromethyl)amine, as represented by the following eqn.[5,6]:

$$(CF_3)\ As + n\ RX \rightarrow (CF_3)_{3-n}AsR_n$$

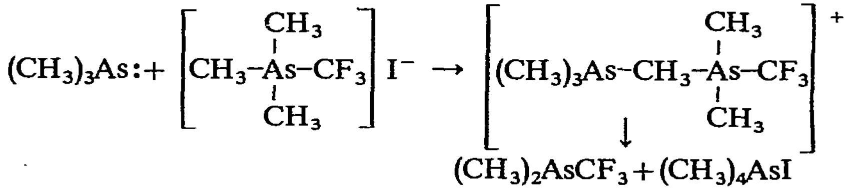
$$[n = 1,2;\ R = CH_3, X = I;\ R = (CF_3)_2N, X = Cl, Br]$$

Such exchange with the halogens are less well defined, and have been reported for chlorine, bromine and iodine. In addition, chlorine also gives pentacovalent arsenic derivatives and the nature of the products depends very much on the conditions used[7].

Bis(trifluoromethyl)nitroxide forms only addition products with tris(trifluoromethyl)phosphine, in contrast to the radical exchange reactions reported with both methyl iodide and *N*-halogenobis(trifluoromethyl)amine. On the other hand, the nitroxide (I) undergoes stepwise substitution reactions with tris(trifluoromethyl)arsine, even to the extent of replacing three CF$_3$ groups, but no pentacovalent addition derivative has been detected. This is the first case in which complete substitution has been observed.

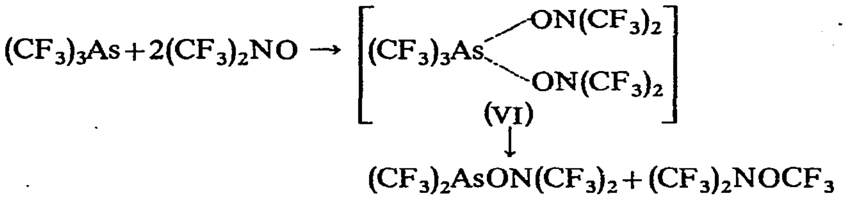
In radical exchange studies of organoarsenic compounds, two mechanisms have been proposed, one or other being favoured according to the nature of the groups bonded to arsenic. For example, the reaction between trimethylphosphine and trifluoromethyl iodide proceeds via the formation of quarternary arsonium iodide intermediate. The presence of a highly electronegative CF$_3$ group would promote a nucleophilic attack on the carbon atom of a methyl group, according to the following scheme[5]:

$$CF_3I + (CH_3)_3As \rightarrow [(CH_3)_3AsCF_3]I$$



$$(CH_3)_3As{:} + \left[\begin{array}{c} CH_3 \\ | \\ CH_3\text{–}As\text{–}CF_3 \\ | \\ CH_3 \end{array}\right] I^- \rightarrow \left[\begin{array}{c} \qquad\qquad\quad CH_3 \\ \qquad\qquad\quad | \\ (CH_3)_3As\text{–}CH_3\text{–}As\text{–}CF_3 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CH_3 \end{array}\right]^+ I^-$$
$$\downarrow$$
$$(CH_3)_2AsCF_3 + (CH_3)_4AsI$$

A different mechanism must be suggested for the reactions of tris(trifluoromethyl)arsine with either methyl iodide, *N*-halogenobis(trifluoromethyl)amine or bis(trifluoromethyl)nitroxide, since the nucleophilic character of tris(trifluoromethyl)arsine is markedly reduced by the presence of highly electronegative trifluoromethyl substituents. A pentacovalent arsenic derivative is postulated in this case:



$$(CF_3)_3As + 2(CF_3)_2NO \rightarrow \left[(CF_3)_3As\begin{matrix}ON(CF_3)_2\\ON(CF_3)_2\end{matrix}\right] \text{(VI)} \rightarrow (CF_3)_2AsON(CF_3)_2 + (CF_3)_2NOCF_3$$

Instead of involving the formation of a pentacovalent intermediate (VI), the reaction could also proceed by addition of one mole of the nitroxide (I) to give a radical intermediate (B), followed by the elimination of a trifluoromethyl radical. The formation of only tris(trifluoromethyl)hydroxylamine instead of hexafluoroethane can be attributed to the effective scavenging ability of the nitroxide. The reactions can be represented as follows:

$$(CF_3)_2NO + (CF_3)_3As \rightarrow (CF_3)_2NO\dot{A}s(CF_3)_3 \text{ (B)}$$

$$(CF_3)_2NO\dot{A}s(CF_3)_3 \rightarrow (CF_3)_2NOAs(CF_3)_2 + {}^{\bullet}CF_3$$

$$(CF_3)_2NO + {}^{\bullet}CF_3 \rightarrow (CF_3)_2NOCF_3$$

It is likely that the reactions proceed both via a pentacovalent and via an arsenic radical intermediate, (B).

EXPERIMENTAL

All manipulations were carried out in a conventional Pyrex vacuum system; all-glass break-seal ampoules were employed as reaction vessels. Vapour-phase IR spectra were recorded on a Perkin–Elmer 337 spectrometer; ^{19}F NMR spectrum was recorded at Cambridge at 40 Mc/sec on a Varian V4300B spectrometer with trichlorofluoromethane as standard.

Tris(trifluoromethyl)arsine was prepared by Brandt, Emeléus and Haszeldine's method[8]. Bis(trifluoromethyl)nitroxide was prepared by the oxidation of bis(trifluoromethyl)hydroxylamine with argentic oxide, and bis(trifluoromethyl)arsine by the reaction of bis(trifluoromethyl)iodoarsine with hydrogen chloride in the presence of mercury[9].

Reaction of bis(trifluoromethyl)nitroxide with elemental arsenic

Bis(trifluoromethyl)nitroxide (1.46 g, 8.70 mmoles) was introduced into an ampoule containing arsenic (0.0623 g, 0.831 mgatom) (which was powdered from arsenic rod) and sealed under vacuum. The mixture was left to stand for two days, and then fractionated to give tris[bis(trifluoromethyl)nitroxy]arsine (IV) (0.363 g, 0.628 mmole; m.p. 29.5°) (Found: F, 59.0, $C_6AsF_{18}N_3O_3$ calcd.: F, 58.91%.) and unreacted bis(trifluoromethyl)nitroxide (1.101 g, 6.55 mmoles); and some residual amount of arsenic (0.0193 g) remained in the ampoule.

The IR spectrum of compound (IV) gave bands at 1387 w, 1303 vs, 1264 vs, 1222 vs, 1038 (sh) 1022 m, 969 m, 793 w, 740 w and 708 w.

Reaction of bis(trifluoromethyl)arsine with bis(trifluoromethyl)nitroxide

Bis(trifluoromethyl)arsine (0.566 g, 3.93 mmoles) and bis(trifluoromethyl)nitroxide (0.516 g, 3.93 mmoles) were sealed in an ampoule under vacuum, which was allowed to warm from −65° to room temperature. The purple colour was completely discharged within half an hour. Vacuum fractionation gave[bis(trifluoromethyl)nitroxy]bis(trifluoromethyl)arsine (II) (0.512 g, 1.34 mmoles) (Found: F, 58.0; mol.wt., 379. $C_4AsF_{12}NO$ calcd.: F, 58.3 %; mol.wt., 381.) and bis(trifluoromethyl)hydroxylamine (0.334 g, 1.98 mmoles). Some unreacted bis(trifluoromethyl)arsine (0.219 g, 1.52 mmoles) was recovered.

The IR spectrum of compound (II) gave bands at 1305 vs, 1257 vs, 1230 vs, 1210 vs, 1198 vs, 1160 vs, 1150 vs, 1128 vs, 1110 vs, 1028 s, 968 s, 798 m, 740 (sh), w, 730 w, 705 m and 578 w. Its ^{19}F NMR spectrum gave $\varphi[(CF_3)As] = 63.0$ ppm and $\varphi[(CF_3)_2NO] = 76.4$ ppm. An appreciable long range F(CN)–F(CAs) coupling (1.4 Hz) was observed, whereupen each peak was split into a 1/6/15/20/15/6/1 septet.

Reactions of tris(trifluoromethyl)arsine and bis(trifluoromethyl)nitroxide

(*a*). A mixture of tris(trifluoromethyl)arsine (0.946 g, 3.56 mmoles) and bis(trifluoromethyl)nitroxide (1.126 g, 6.70 mmoles) was left to stand in a sealed ampoule at room temperature for 15 h. Trap-to-trap fractionation afforded (*i*) bis[bis(trifluoromethyl)nitroxy]trifluoromethylarsine (III) (0.142 g, 0.296 mmoles) (Found: F, 58.78. $C_5F_{15}AsN_2O_2$ calcd.: F, 59.34%.), (*ii*) [bis(trifluoromethyl)nitroxy]bis(trifluoromethyl)arsine (0.709 g, 1.86 mmoles) (Found: mol.wt., 388. $C_4AsF_{12}NO$ calcd.: mol.wt., 381.)—confirmed by its IR spectrum with that of an authentic material—and (*iii*) tris(trifluoromethyl)hydroxylamine (1.190 g, 5.021 mmoles). (Found: mol.wt., 240. C_3F_9ND calcd.: mol.wt., 237.)

The IR absorptions of compound (III) are located at 1305 s, 1257 vs, 1230 vs, 1210 vs, 1198 vs, 1160 vs, 1150 vs, 1128 vs, 1110 vs, 1028 s, 908 s, 798 m, 740 (sh) w, 730 w, 578 w.

(*b*). Tris(trifluoromethyl)arsine (0.441 g, 1.56 mmoles) and bis(trifluoromethyl)nitroxide (1.052 g, 6.26 mmoles) were allowed to react in a sealed ampoule for 2 days. The products obtained were (*i*) tris[bis(trifluoromethyl)nitroxy]arsine (0.0154 g, 0.027 mmole) found at 0° trap, (*ii*) bis[bis(trifluoromethyl)nitroxy]trifluoromethylarsine (0.709 g, 1.45 mmoles) trapped at −20° and (*iii*) tris(trifluoromethyl)hydroxylamine (0.742 g, 3.13 mmoles).

Both the arsenic derivatives were confirmed by their IR spectra.

(*c*). A mixture of tris(trifluoromethyl)arsine (0.477 g, 1.69 mmoles) and the nitroxide (1.82 g, 10.8 mmoles) was heated in a sealed ampoule at 70° for 40 h. Fractionation afforded tris[bis(trifluoromethyl)nitroxy]arsine trapped at 0° (0.890 g, 1.54 mmoles, m.p. 29.5°), tris(trifluoromethyl)hydroxylamine (1.11 g, 4.68 mmoles) and unreacted nitroxide (I) (0.261 g, 1.55 mmoles).

Reactions of tris[bis(trifluoromethyl)nitroxy]arsine (IV) with hydrogen chloride

The arsine derivative (IV) (0.125 g, 0.217 mmole) and hydrogen chloride (0.017 g, 0.477 mole) were set aside in a sealed ampoule at room temperature overnight. Fractionation gave arsenic trichloride (0.0421 g, 0.231 mmole) (Found: Cl, 58.4. $AsCl_3$ calcd.: 58.6 %.), collected from −64° trap and bis(trifluoromethyl)hydroxylamine (0.0957 g, 0.556 mmole) collected from −86° trap.

In another experiment, 0.844 g (1.46 mmoles) of the arsine (IV) and 0.0578 g (1.58 mmoles) of hydrogen chloride were allowed to react overnight. The reaction afforded bis[bis(trifluoromethyl)nitroxy]chloroarsine (V) (0.223 g, 0.500 mmole) (Found: Cl, 8.45. $C_4AsClF_{12}N_2O_2$ calcd.: Cl, 7.95%.) and bis(trifluoromethyl)-hydroxylamine (0.372 g, 2.20 mmoles). Unreacted tris-arsine (IV) (0.190 g, 0.329 mmole) was recovered at −20° trap.

IR spectrum of compound (V) gave the following peaks: 1390 w, 1320 s, 1260 vs, 1225 vs, 1026 s, 975 s, 800 m and 715 m cm^{-1}.

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