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Novel condensation reactions of *O*-nitrosobis(trifluoromethyl)hydroxylamine and trifluoronitrosomethane with arsine

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Abstract

N-Bis(trifluoromethyl)nitroxy-iminoarsine, $(CF_3)_2NON{=}AsH$, is formed by a condensation reaction between *O*-nitrosobis(trifluoromethyl)hydroxylamine and arsine. It undergoes reactions with $(CF_3)_2NO$ to afford $(CF_3)_2NON{=}AsON(CF_3)_2$ and bis(trifluoromethyl)hydroxylamine. Both the iminoarsines $(CF_3)_2NON{=}AsR$ ($R{=}H$, $(CF_3)_2NO$) undergo addition reactions across the N=As bond with HI to give $(CF_3)_2NONHAsIR$. The reaction of trifluoronitrosomethane and arsine follows a similar pathway, affording an unstable iminoarsine, $CF_3N{=}AsH$, which decomposes via a free-radical mechanism even at low temperatures.

Introduction

Extensive interest has developed in recent years regarding the chemistry of unsaturated compounds of the p-block elements with low coordination numbers. Within the Group 15 elements, a number of stable phosphorus derivatives which have been synthesized contain the following p_π–p_π bonds: P=C, P=N, P=P, P=As and P=Sb, P=Si and P=Ge [1–6]. Some X-ray data of the compounds RP=PR (where $R = C(SiMe_3)_3$ and $2,4,6\text{-}Bu^t_3C_6H_2$) are now available [7, 8]. The stability of such compounds has been attributed to the presence of bulky substituents like Bu^t, Me_3Si, $(Me_3Si)_2N$ and $2,4,6\text{-}Bu^t_3C_6H_2$ which shield the reactive sites [3].

Until now, no examples have been provided of 2-coordinate iminoarsines. We now report in detail our findings on the synthesis and characterisation of these compounds, the results having been reported earlier as preliminary communications [9, 10].

Results and discussion

The reactions of trifluoronitrosomethane and *O*-nitrosobis(trifluoromethyl)hydroxylamine with arsine in a 1:1 molar ratio give *N*-trifluoromethyl-iminoarsine and *N*-bis(trifluoromethyl)nitroxy-iminoarsine, respectively according to the equation:

$$AsH_3 + RNO \longrightarrow RN{=}AsH + H_2O$$

(where $R = CF_3$, $(CF_3)_2NO$).

The reactions of trifluoronitrosomethane with arsine in a 1:1 molar ratio occurred at −120 °C to afford *N*-trifluoromethyl-iminoarsine, $CF_3N{=}AsH$ (A), in 14% yield together with water.

Iminoarsine A was isolated in a −126 °C trap as a white solid (and water in a −60 °C trap) on trap-to-trap vacuum fractionation. The iminoarsine began to decompose even at temperatures as low as −110 °C. On standing for *c.* 4 min at room temperature, the compound decomposed to afford a black metallic film of arsenic metal, trifluoromethane and a non-condensable gas which was presumably nitrogen. A fast scan of the IR spectrum of iminoarsine A gave peaks located at 2234 (νAs–H); 1319, 1285 and 1222 (νC–F); 994 (νC–N); 873 (νAs=N); and 724 (δC–F) cm^{-1}.

Iminoarsine A is therefore unstable under ambient conditions, and the decomposition products can be rationalised in terms of the following free-radical mechanism:

$$CF_3N{=}AsH \longrightarrow CF_3^{\cdot} + H^{\cdot} + As + 1/2N_2$$

$$CF_3^{\cdot} + H^{\cdot} \longrightarrow CF_3H$$

The reaction of *O*-nitrosobis(trifluoromethyl)hydroxylamine with arsine occurs at room temperature to give *N*-bis(trifluoromethyl)nitroxy-iminoarsine, $(CF_3)_2NON{=}AsH$ (B). No water was isolated but a dark brown solid which is hygroscopic was also formed in the reaction ampoule. The iminoarsine B obtained

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in *c.* 42% yield was isolated in the −86 °C trap (passing the −60 °C trap) as a white solid on trap-to-trap vacuum fractionation. Its IR spectrum showed the following absorption bands: 2238 (νAs–H); 1322, 1273, 1245, 1186 (νC–F); 1070 (νN–O); 972 (νC–N); and 721 (νC–F) cm^{-1}. A band at 869 cm^{-1} was assigned as the As=N stretching vibration.

The EI-MS (70 eV) of iminoarsine B did not exhibit the parent ion but gave other fragmentation ions at *m/z* 170 $[CF_2NONAsH]^{+\cdot}$; *m/z* 154 $[CF_2N_2AsH]^{+\cdot}$; *m/z* 119 $[AsON]^{+\cdot}$; and *m/z* 69 $[CF_3]^{+\cdot}$. The molecular weight determined by Regnault's method was 258 g mol^{-1} (calc. 258 g mol^{-1}).

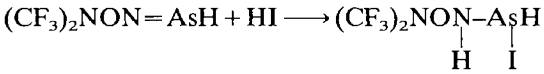
The reaction of *N*-bis(trifluoromethyl)nitroxyiminoarsine and bis(trifluoromethyl)nitroxyl resulted in hydrogen abstraction of the As–H hydrogen to give a quantitative yield of *N,N*-bis(trifluoromethyl)hydroxylamine. The bis(trifluoromethyl)nitroxy derivative $(CF_3)_2NON{=}AsON(CF_3)_2$ was obtained in 52% yield.

$$(CF_3)_2NON{=}AsH + 2(CF_3)_2NO \longrightarrow$$

$$(CF_3)_2NON{=}AsON(CF_3)_2\ (C) + (CF_3)_2NOH$$

Compound C was trapped as a pale yellow solid at the −70 °C trap (passing the −60 °C trap) and became a volatile colourless liquid at room temperature. It showed characteristic IR absorptions for the $(CF_3)_2NO$ group at 1291, 1244, 1199 (νC–F); 1080 (νN–O); and 772 (νC–F) cm^{-1}. The As=N stretching vibration was located at 869 cm^{-1}. Its EI-MS showed fragment ions at *m/z* 168 $[(CF_3)_2NO]^{+\cdot}$; 75 $[As]^{+\cdot}$ and 69 $[CF_3]^{+\cdot}$. Its molecular weight as determined by Regnault's method was 425 g mol^{-1} (compound C requires 425 g mol^{-1}).

Iminoarsine B underwent addition reactions across the As=N bond with hydrogen iodide.

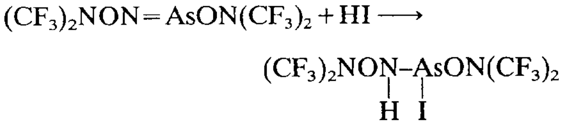


$$(CF_3)_2NON{=}AsH + HI \longrightarrow (CF_3)_2NO\underset{H}{N}{-}\underset{I}{As}H\ (D)$$

Isolated in 75% yield in the −60 °C trap (passing the −40 °C trap) as a pale yellow solid, compound D is a colourless liquid at room temperature. It turned slightly brown due to decomposition to give iodine on standing. The IR spectrum showed the presence of the N–H and As–H group at 3398 and 2272 cm^{-1}, respectively. The $(CF_3)_2NO$ group absorptions were detected at 1323, 1271, 1240, 1213, 1184 (νC–F); 1068 (νN–O); 972 (νC–N); and 717 (νC–F) cm^{-1}. The EI-MS (70 eV) gave fragmentation peaks at *m/z* 218 $[HNAsHI]^{+}$; 217 $[NAsHI]^{+\cdot}$; 168 $[C_2F_6NO]^{+\cdot}$; 149 $[C_2F_5NO]^{+\cdot}$; 130 $[C_2F_4NO]^{+\cdot}$; 127 $[I]^{+\cdot}$; and 69 $[CF_3]^{+\cdot}$. The addition product was unstable to light and decomposed to give iodine.

The ^{19}F NMR spectrum of compound D showed a singlet at 16.39 ppm with respect to CF_3COOH which is attributed to the CF_3 group. The ^{1}H NMR spectrum exhibited two sets of multiplets: 0.40 (δAsH); and 6.13 (δNH) ppm with respect to TMS.

Iminoarsine C reacted with anhydrous hydrogen iodide in a similar manner to B:



$$(CF_3)_2NON{=}AsON(CF_3)_2 + HI \longrightarrow (CF_3)_2NO\underset{H}{N}{-}\underset{I}{As}ON(CF_3)_2\ (E)$$

Compound E was trapped as a yellow liquid in the −60 °C trap (passing the −40 °C trap) in 85% yield. It was decomposed by light at room temperature to give iodine. Its IR spectrum showed absorptions at 3415 (N–H); 1312, 1269, 1226 (νC–F); 1046 (νN–O); 972 (νC–N); and 712 (νC–F) cm^{-1}. Its EI-MS shows fragment ions at *m/z* 257 $[C_2F_6NONAs]^{+\cdot}$; 168 $[C_2F_6NO]^{+\cdot}$; 149 $[C_2F_5NO]^{+\cdot}$; and 69 $[CF_3]^{+\cdot}$.

The addition reactions of both iminoarsines were marked by the disappearance of the As=N stretching vibration at 869 cm^{-1} for the products D and E.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 983G infrared spectrometer. Mass spectra were recorded on a Micromass mass spectrometer. Nuclear magnetic resonance (NMR) data were obtained using a 200 MHz Jeol NMR spectrometer. Elemental analyses were undertaken by the Microanalytical Laboratory, National University of Singapore.

Reaction of trifluoronitrosomethane with arsine in a 1:1 molar ratio

Trifluoronitrosomethane (0.2759 g, 2.78 mmol) and arsine (0.2212 g, 2.80 mmol) were sealed *in vacuo* in a Pyrex glass ampoule. The ampoule was then transferred to a −126 °C slush bath. A gradual disappearance of the blue colouration of CF_3NO was observed. At −110 °C, brownish stains commenced to form on the sides of the reaction tube. The reaction mixture was quickly subjected to trap-to-trap fractionation using −60 °C, −96 °C, −126 °C and −196 °C slush baths. The iminoarsine $CF_3N{=}AsH$ was isolated in the −126 °C slush bath in 14% yield. The iminoarsine decomposed on standing in an evacuated ampoule at room temperature for *c.* 4 min to give a metallic black deposit of arsenic metal on the side of the ampoule. Vacuum trap-to-trap fractionation of the decomposition products gave (a) a non-condensable gas, presumably nitrogen, and (b) a volatile gas trapped at liquid nitrogen trap, whose IR spectrum gave absorptions at 2911 (w); 1370 (w); 1209 (s); 1162 (s); and 720 (m) cm^{-1} which are identical to those of fluoroform (Analysis: Found: M,

70. CF_3H requires: M, 70). Analysis showed that the metallic substance is arsenic metal.

Reaction of O-nitrosobis(trifluoromethyl)hydroxylamine with arsine in a 1:1 molar ratio

O-Nitrosobis(trifluoromethyl)hydroxylamine (0.4670 g, 0.24 mmol) and arsine (0.1842 g, 0.24 mmol) were condensed in a Pyrex glass reaction tube and allowed to warm to room temperature from −126 °C. On attaining room temperature, the orange colour of the hydroxylamine persisted for 30 min before discharge. The reaction mixture was immediately fractionated using −60 °C, −96 °C, −126 °C and −196 °C slush baths. A product mixture was obtained at the −96 °C bath and was re-fractionated with −60 °C, −86 °C and −196 °C baths. A trace amount of $(CF_3)_2NONO$ was obtained in the −196 °C slush bath while the iminoarsine $(CF_3)_2NON{=}AsH$ (A) was obtained in the −86 °C slush bath in 42% yield.

Reaction of N-bis(trifluoromethyl)nitroxy-iminoarsine with bis(trifluoromethyl)nitroxyl in a 1:2 molar ratio

N-Bis(trifluoromethyl)nitroxy-iminoarsine (0.3430 g, 1.33 mmol) and bis(trifluoromethyl)nitroxyl (0.4461 g, 2.63 mmol) were condensed in a Pyrex glass ampoule and allowed to warm to room temperature from −96 °C. After 18 h, the colour of the solution had completely disappeared and a colourless liquid had been formed. The reaction products were fractionated at −60 °C, −96 °C, −126 °C and −196 °C. A product mixture was obtained in the −96 °C bath. The mixture was re-fractionated using −60 °C, −70 °C, −96 °C and −196 °C slush baths. A quantitative yield of bis(trifluoromethyl)hydroxylamine was obtained in the −96 °C slush bath while the iminoarsine $(CF_3)_2NON{=}AsON(CF_3)_2$ was obtained in the −70 °C slush bath in 52% yield.

Reaction of N-bis(trifluoromethyl)nitroxy-iminoarsine with anhydrous hydrogen iodide in a 1:1 molar ratio

A mixture of *N*-bis(trifluoromethyl)nitroxy-iminoarsine (0.4105 g, 1.59 mmol) and anhydrous hydrogen iodide (0.2070 g, 1.60 mmol) was condensed in a Pyrex glass ampoule. The reaction mixture was kept in the dark at room temperature for 2 h, after which some iodine started to form. The reaction products were fractionated using −40 °C, −60 °C and −196 °C slush baths. $(CF_3)_2NONHAsHI$ was obtained in 75% yield in the −60 °C trap. (Analysis: Found: I, 33.02%. $C_4FH_6N_2O_2AsI$ requires: I, 32.90%.)

Reaction of $(CF_3)_2NON{=}AsON(CF_3)_2$ with anhydrous hydrogen iodide in a 1:1 molar ratio

The iminoarsine $(CF_3)_2NON{=}AsON(CF_3)_2$ (0.0589 g, 0.13 mmol) and anhydrous hydrogen iodide (0.0166 g, 0.14 mmol) were condensed in a Pyrex glass ampoule which was shielded from light. The reaction proceeded at room temperature with the formation of a pale yellow liquid. Fractionation of the reaction products was effected after standing for 24 h using −60 °C, −96 °C, −126 °C and −196 °C slush baths. A reaction product mixture was obtained in the −60 °C slush bath. This was purified by fractionation using −40 °C, −60 °C, −96 °C and −196 °C slush baths. The compound $(CF_3)_2NONHAs(I)ON(CF_3)_2$ was obtained in the −60 °C bath in 85% yield. (Analysis: Found: I, 22.07. $C_4F_{12}HN_3O_2AsI$ requires: I, 22.96%.)

Conclusions

$(CF_3)_2NON{=}AsH$, obtained via a novel condensation reaction, is the first example of a 2-coordinate iminoarsine. In addition to the IR spectrum, the structure of the N=AsH group is supported by both the substitution reaction with the $(CF_3)_2NO$ radical and the addition reaction with HI. In contrast, the iminoarsine $CF_3N{=}AsH$ is found to decompose at low temperatures via a free-radical mechanism to give CF_3H and arsenic metal.

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