Synthesis of *NN*-dimethyl-*N'N'*-bis(trifluoromethyl)arsinohydrazine

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WHILE aminoarsines $R^1_xN(AsR^2_3)_{3-x}$ (R^1 = H, alkyl, or aryl; R^2 = alkyl or aryl) are a well established class of nitrogen–arsenic compounds,[1] related systems with other substituents on the nitrogen atom of the amino-group are little known, beyond phosphinoaminoarsines $(CF_3)_2P{\cdot}NR{\cdot}As{\cdot}(CF_3)_2$ (R = H, CH_3) reported by Burg,[2] and silylaminoarsines, $(Me_3Si)_2N{\cdot}AsMe_2$.[3] We report here the first synthesis and isolation of such an *N*-substituted aminoarsine, *NN*-dimethyl-*N'N'*-bis(trifluoromethyl)arsinohydrazine, $Me_2N{\cdot}NHAs(CF_3)_2$ (I), where the substituent on nitrogen is the dimethylamino-group. Compound (I) was obtained in high yield at low temperature by reaction between $(CF_3)_2AsCl$ and $Me_2N{\cdot}NH_2$ in ether solution. The measured molar ratios of the individual reactants used and products formed determined the following stoicheiometry:

$$(CF_3)_2AsCl + 2Me_2N{\cdot}NH_2 \rightarrow$$
$$Me_2N{\cdot}NHAs(CF_3)_2 + (CH_3)_2N{\cdot}NH_2,HCl$$

Compound (I) has M_{obs} 275, 272; M_{calc} 272, b.p. 20°/14·6 mm.; m.p. 3·0°.

An 80% yield of pure product, based on $(CF_3)_2AsCl$, was obtained

While the pure compound (I) (a white solid) melted sharply at 3·0° to a colourless liquid, a supercooled liquid exhibiting an intense yellow colour could be obtained. Compound (I) was identified by vapour-phase molecular-weight measurements, by ^1H and ^{19}F n.m.r. and infrared spectroscopy. The proton n.m.r. spectrum consisted of two resonance absorptions in approximately 6:1 ratio, corresponding to six equivalent protons on the two methyl groups [at τ 7·50; reference: internal $SiMe_4$] and one proton on the nitrogen atom (τ 5·73). The ^{19}F resonance consisted of a single absorption (δ + 57·25 p.p.m., reference: external $CFCl_3$) which remained sharp ($\Delta\nu_{\frac{1}{2}}$ = 6·0 Hz) from +30° to −50°, consistent with rapid quadrupolar relaxation of the spin-$^3/_2$ ^{75}As nucleus, and free rotation about the N–As bond. Thus we could not detect any significant $N(p_\pi)$–$As(d_\pi)$ dative bonding in the structure. Together, the ^1H and ^{19}F n.m.r. spectra preclude alternative formulations that could arise as the result of methyl, H, or CF_3 migration or molecular rearrangement during the synthesis. In addition, the presence of a secondary amino-grouping, >N–H, was indicated in the infrared spectrum, together with absorption bands due to methyl, CF_3, and N–N.

Compound (I) decomposed slowly at room temperature, more rapidly at 80°, liberating equivalent molar amounts of nitrogen and fluoroform to yield yellow nonvolatile products. Reaction of (I) with anhydrous HCl cleaved the As–N bond giving $(CF_3)_2AsCl$ and $Me_2N{\cdot}NH_2{\cdot}HCl$ quantitatively, further confirming our formulation.

The potential multidentate character of this N–N–As system is being investigated.

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