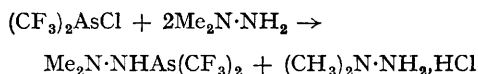


## Synthesis of *NN*-dimethyl-*N'N'*-bis(trifluoromethyl)arsinohydrazine

By L. K. PETERSON\* and K. I. THÉ

(Department of Chemistry, Simon Fraser University, Burnaby 2, B.C., Canada)

WHILE aminoarsines  $R^1N(AsR^2)_3-x$  ( $R^1 = H$ , alkyl, or aryl;  $R^2 =$  alkyl or aryl) are a well established class of nitrogen-arsenic compounds,<sup>1</sup> 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,<sup>2</sup> and silylaminoarsines,  $(Me_3Si)_2N \cdot AsMe_2$ .<sup>3</sup> 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 stoichiometry:



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 <sup>1</sup>H and <sup>19</sup>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  $\tau$  7.50; reference: internal  $SiMe_4$ ] and one proton on the nitrogen atom ( $\tau$  5.73). The <sup>19</sup>F resonance consisted of a single absorption ( $\delta + 57.25$  p.p.m., reference: external  $CFCl_3$ ) which remained sharp ( $\Delta\nu_{1/2} = 6.0$  Hz) from +30° to -50°, consistent with rapid quadrupolar relaxation of the spin- $3/2$  <sup>75</sup>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 <sup>1</sup>H and <sup>19</sup>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 fluorine 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.

We thank Dr. E. J. Wells for assistance with n.m.r. studies, and N.R.C. for a research grant.

(Received, September 5th, 1967; Com. 953.)

<sup>1</sup> W. R. Cullen, *Adv. Organometallic Chem.*, 1966, **4**, 145; and references therein.

<sup>2</sup> J. Singh and A. B. Burg, *J. Amer. Chem. Soc.*, 1966, **88**, 718.

<sup>3</sup> O. J. Scherer and M. Schmidt, *Angew. Chem.*, 1964, **76**, 144.