Aminoarsines: Their Use in the Synthesis of Organoarsenic Heterocycles

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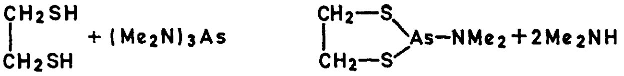
Summary Aminoarsines have been found to have a wide application in the preparation of organoarsenic heterocycles in high yields at ambient temperatures.

IN comparison with aminophosphines, aminoarsines have been little studied. Our interest in amino-derivatives of metals and semi-metals has necessitated the preparation of heterocyclic organoarsenic compounds.

Aminoarsines, *e.g.* trisdimethylaminoarsine, are very reactive compounds and as such are valuable intermediates. They react with protic species, *e.g.* hydrogen halides,[1] and unsaturated substrates, *e.g.* isocyanates.[2] Recently they have been used successfully in the synthesis of enamines by their reaction with ketones.[3]

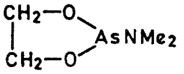
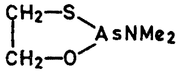
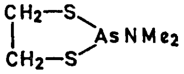
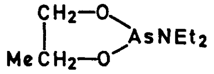
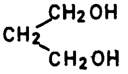
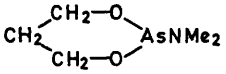
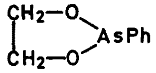
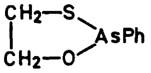
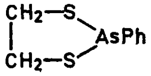


We have found that aminoarsines react readily with difunctional organic compounds, such as diols, dithiols, and thiol-alcohols, to give in many cases high yields, at ambient temperatures, of the corresponding organoarsenic heterocycle. The scope of this reaction is typified by a selection of the range of organoarsenic heterocycles (Table) prepared by this method.

A typical reaction sequence is as follows: Ethanedithiol (0·79 g.) was added to bisdiethylaminophenylarsine (2·25 g.) in petroleum (25 ml, 40—60 b.p.) at room temperature. The mixture was refluxed for ½ hr. After removal of the volatile materials the residue on distillation afforded 2-phenyl-1,3,2-dithioarsolan (1·59 g., 96%).

The ease of this type of reaction can be attributed to (a) the volatility of the secondary amine formed in the reaction and (b) the stability of As–S bonds in the relevant cases.

TABLE

Reactants	Product	Yield (%)
$\begin{array}{l}CH_2OH\\ \vert\\ CH_2OH\end{array} + (Me_2N)_3As$		45
$\begin{array}{l}CH_2SH\\ \vert\\ CH_2OH\end{array} + (Me_2N)_3As$		65
$\begin{array}{l}CH_2SH\\ \vert\\ CH_2SH\end{array} + (Me_2N)_3As$		62
$\begin{array}{l}CH_2OH\\ \vert\\ MeCH_2OH\end{array} + (Et_2N)_3As$		48
 + $(Me_2N)_3As$		40
$\begin{array}{l}CH_2OH\\ \vert\\ CH_2OH\end{array} + PhAs(NEt_2)_2$		90
$\begin{array}{l}CH_2SH\\ \vert\\ CH_2OH\end{array} + PhAs(NEt_2)_2$		98
$\begin{array}{l}CH_2SH\\ \vert\\ CH_2SH\end{array} + PhAs(NEt_2)_2$		96

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[2] G. Oertel, H. Malz, and H. Holtschmidt, *Chem. Ber.*, 1964, **97**, 891.
[3] G. Manoussakis, *J. Inorg. Nuclear Chem.*, 1968, **30**, 3100.