The arsine derivatives of cadmium halides are stable, colourless, crystalline compounds. The following table contains a list of the compounds isolated, together with their melting points:

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.P.</th>
</tr>
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<tbody>
<tr>
<td>Phenyl dimethyl arsine cadmium chloride</td>
<td>220° C</td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
<td></td>
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</tr>
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<td></td>
<td>p-</td>
</tr>
</tbody>
</table>

In the phenyl dimethyl arsine compounds it will be noticed that the melting point rises from iodide to chloride, corresponding to the variation in melting point of the cadmium halides themselves. The compounds are all soluble in methyl and ethyl alcohols and in acetone, the iodide being the most soluble, particularly in acetone. Furthermore, with the exception of the iodides, solution is accompanied by decomposition, the arsine being apparently removed. The compounds could not be recrystallised. In order to recover the compound it is necessary to add excess of the arsine. Stability towards ether and benzene is in the same direction, but towards water or nitric acid the chloride is the most stable and the iodide the least, the latter decomposing in the cold, the former only on warming.

Experimental.

Phenyl dimethyl arsine cadmium chloride, Cd(PhMe₂As)Cl₂, was prepared by adding a hot alcoholic solution of the arsine to cadmium chloride dissolved in a large volume of hot alcohol. On cooling the compound slowly separated in fine colourless needles melting at 220° C.

Found: Cd=31.3, 0.1% per cent.
Cd₈H₈AsCl₂Cd requires Cd=30.9, Cl =0.1% per cent.

Phenyl dimethyl arsine cadmium bromide, Cd(PhMe₂As)Br₂, was prepared by mixing hot alcoholic solutions of the arsine and cadmium bromide and allowing to cool. After several hours a crystalline precipitate of cadmium bromide was removed, and the nitrate allowed to stand. A further precipitate of cadmium bromide was removed after twenty-four hours, and the solution allowed to stand for several weeks. Crystals gradually appeared, sometimes in the form of needles.

In a previous communication Anderson and Burrows (Proc. Roy. Soc. N.S.W., 1936, 70, 63-68) described compounds obtained from mercury salts and tertiary arsines. It was shown that two types of compound could be obtained, HgX₂R and HgX₂R₂, where R represents a molecule of tertiary arsine. It was found impossible to isolate a compound containing more than two molecules of arsine combined with one of a mercuric salt. Zinc and cadmium halides resemble those of mercury as regards their solubilities in organic liquids; the elements also have low atomic volumes. It was therefore decided to examine the compounds that could be obtained from cadmium and zinc salts with phenyl dimethyl arsine, diphenyl methyl arsine, and o- and p-tolyl dimethyl arsines. The cadmium derivatives are described in the present communication.

Compounds of cadmium halides with ammonia have been described containing one, two, three, four or six molecules of ammonia. These have generally been obtained in the dry way from the solid halide and ammonia. The most staple of these is of the type [Cd(NH₃)₄]X₂, which can be prepared in solution. In view of the stability of the 4-covalent complex cadmium ion it was thought that similar compounds containing one molecule of a cadmium halide coordinated with four molecules of a tertiary arsine might be obtained. Such, however, was not the case. Varying quantities of arsine were taken up to six molecules of arsine to one of cadmium halide. With the exception of bis-diphenyl methyl arsine cadmium iodide Cd(Ph₂MeAs)₂I₂, in which two molecules of arsine are coordinated with one of cadmium, all of the compounds isolated contain one molecule of arsine to one of cadmium halide.
The arsine derivatives of cadmium halides are stable, colourless, crystalline compounds. The following table contains a list of the compounds isolated, together with their melting points:

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<td>186° C.</td>
</tr>
<tr>
<td>&quot; &quot; &quot; &quot; &quot; iodide</td>
<td>108° C.</td>
</tr>
<tr>
<td>Diphenyl methyl arsine cadmium chloride</td>
<td>292° C.</td>
</tr>
<tr>
<td>&quot; &quot; &quot; &quot; &quot; bromide</td>
<td>257° C.</td>
</tr>
<tr>
<td>Bis-diphenyl &quot; &quot; &quot; iodide</td>
<td>100° C.</td>
</tr>
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<td>o-tolyl dimethyl arsine cadmium iodide</td>
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In the phenyl dimethyl arsine compounds it will be noticed that the melting point rises from iodide to chloride, corresponding to the variation in melting point of the cadmium halides themselves.

The compounds are all soluble in methyl and ethyl alcohols and in acetone, the iodide being the most soluble, particularly in acetone. Furthermore, with the exception of the iodides, solution is accompanied by decomposition, the arsine being apparently removed. The compounds could not be recrystallised. In order to recover the compound it is necessary to add excess of the arsine. Stability towards ether and benzene is in the same direction, but towards water or nitric acid the chloride is the most stable and the iodide the least, the latter decomposing in the cold, the former only on warming.

**Experimental.**

*Phenyl dimethyl arsine cadmium chloride*, Cd(PhMe₂As)Cl₂, was prepared by adding a hot alcoholic solution of the arsine to cadmium chloride dissolved in a large volume of hot alcohol. On cooling the compound slowly separated in fine colourless needles melting at 220° C.

Found: Cd = 31·3, Cl = 19·5 per cent.

C₈H₁₁AsCl₂Cd requires Cd = 30·9, Cl = 19·5 per cent.

*Phenyl dimethyl arsine cadmium bromide*, Cd(PhMe₂As)Br₂, was prepared by mixing hot alcoholic solutions of the arsine and cadmium bromide and allowing to cool. After several hours a crystalline precipitate of cadmium bromide was removed, and the filtrate allowed to stand. A further precipitate of cadmium bromide was removed after twenty-four hours, and the solution allowed to stand for several weeks. Crystals gradually appeared, sometimes in the
form of large prisms and sometimes as fine feathery needles. The crystals melted at 186° C.

Found: Cd = 25·4, Br = 35·4 per cent.

\[ \text{C}_8\text{H}_{11}\text{AsBr}_2\text{Cd} \] requires Cd = 24·8, Br = 35·2 per cent.

**Phenyl dimethyl arsine cadmium iodide, Cd(PhMe}_3\text{As})_2\text{I}_2,\)** was prepared by mixing alcoholic solutions of the arsine and cadmium iodide, concentrating on a water bath, and allowing to stand. After several hours colourless long prismatic crystals separated. These were filtered, washed with ether and recrystallised from alcohol and the product was found to melt at 108° C.

Found: Cd = 20·2, I = 46·3 per cent.

\[ \text{C}_9\text{H}_{13}\text{AsI}_2\text{Cd} \] requires I = 45·6 per cent.

**o-tolyl dimethyl arsine cadmium iodide, o-C}_7\text{H}_7\text{Me}_2\text{AsCdI}_2,\)** was obtained by mixing hot concentrated alcoholic solutions of the arsine and cadmium iodide and allowing to stand. The compound separated in needles which were washed with alcohol, and on drying melted at 187° C.

Found: I = 45·3 per cent.

\[ \text{C}_9\text{H}_{13}\text{AsI}_2\text{Cd} \] requires I = 45·6 per cent.

**p-tolyl dimethyl arsine cadmium iodide, p-C}_7\text{H}_7\text{Me}_2\text{AsCdI}_2,\)** prepared in a manner similar to the last compound, crystallised in thick prisms melting at 126° C.

Found: I = 45·4 per cent.

\[ \text{C}_9\text{H}_{13}\text{AsI}_2\text{Cd} \] requires I = 45·6 per cent.

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**Diphenyl methyl arsine cadmium chloride, Cd(Ph}_2\text{Me}_3\text{As})_2\text{Cl}_2.** An alcoholic solution of cadmium chloride was mixed with one of diphenyl methyl arsine and the mixture concentrated on the water bath and allowed to cool. After several hours colourless needles separated. They were removed by filtration, washed with alcohol and air dried. The compound melted at 292° C.

Found: Cl = 16·8 per cent.

\[ \text{C}_{13}\text{H}_{13}\text{AsCl}_2\text{Cd} \] requires Cl = 16·6 per cent.

**Diphenyl methyl arsine cadmium bromide, Cd(Ph}_2\text{Me}_3\text{As})_2\text{Br}_2.** was exceedingly difficult to prepare and was obtained only in small quantity. Cadmium bromide and the arsine (50% excess) were dissolved on the water bath in a large volume of alcohol, and then allowed to stand for several hours at room temperature. Cadmium bromide separated out and was removed by filtration. After several days fine prisms separated from the filtrate in small quantity. After careful washing with alcohol and drying at room temperature these were found to melt at 257° C.

Found: Br = 31·1 per cent.

\[ \text{C}_{13}\text{H}_{13}\text{AsBr}_2\text{Cd} \] requires Br = 31·0 per cent.

**Bis-diphenylmethylarsine cadmium iodide, Cd(Ph}_3\text{MeAs})_2\text{I}_2.** This was the only compound that could be obtained when cadmium iodide was treated with the arsine, although the relative molecular proportions were varied over a wide range. To obtain the pure compound, equimolecular proportions of the constituents were dissolved in hot alcohol and the solutions mixed. On cooling, glistening long prisms separated in a few hours. These were removed
by filtration, washed with alcohol and dried at room temperature. The melting point was 100° C.

Found: I = 29.5 per cent.
C_{28}H_{26}As_{2}I_{2}Cd requires I = 29.8 per cent.

\( o\)-tolyl dimethyl arsine cadmium iodide, o-C_{7}H_{7}Me_{2}AsCdI_{2},
was obtained by mixing hot concentrated alcoholic solutions of the arsine and cadmium iodide and allowing to stand. The compound separated in needles which were washed with alcohol, and on drying melted at 187° C.

Found: I = 45.3 per cent.
C_{9}H_{13}AsI_{2}Cd requires I = 45.6 per cent.

\( p\)-tolyl dimethyl arsine cadmium iodide, p-C_{7}H_{7}Me_{2}AsCdI_{2},
prepared in a manner similar to the last compound, crystallised in thick prisms melting at 126° C.

Found: I = 45.4 per cent.
C_{9}H_{13}AsI_{2}Cd requires I = 45.6 per cent.

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