Oxidative Addition Reactions of Triarylarsines & Triarylstibines with Copper(II) & Mercury(II) Salts

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Oxidative addition reactions of triaryl-arsines and -stibines with anhydrous Hg(II) or Cu(II) salts containing chloride, bromide, iodide, thiocyanate and acetate anions have been found to give triaryl-arsenic and -antimony dihalides, dipseudohalides and diacetates. In this reaction Cu/Hg are reduced to monovalent state.

The reactions of chlorides of Cu(II), Fe(III), Ti(III) have been briefly reported to convert triphenyl-arsines and -stibines to the corresponding dichlorides [Ph₃M₂Cl₂]. In continuation of our work on oxidative addition reaction of Ar₃M compounds (Ar = Ph or p-tol.; M = As or Sb) with interhalogens and pseudohalogens, we now wish to report the reactions of metallic salts M'X₂ (M' = Cu(II), Hg(II); X = Cl, Br, I, NCS, CH₃COO) with triaryl-arsines and -stibines. The Cu(II) and Hg(II) salts are in the process reduced to the monovalent state.

Triphenyl- and tri-p tolyl-arsines and -stibines were obtained by Wurtz reaction of anhydrous metallic trihalides and the appropriate arylhalides in refluxing benzene in the presence of sodium. All the anhydrous metallic salts (AR) were dried before use. Mercuric thiocyanate was prepared by the published method.

A representative reactions is given below, data for other reactions are summarized in Table 1.

Reaction of triphenyl-stibine with mercuric chloride in 1:2 molar ratio — A solution of triphenylstibine (3.01 g; 0.0085 mol) in dried acetone (40 ml) was refluxed with mercuric-chloride (4.82 g; 0.0177 mol) for 4 hr. The white residue of mercurous chloride (Hg₂Cl₂; 3.8 g) and the unreacted excess of mercuric chloride were filtered off. The filtrate on evaporation yielded crude triphenylantimonydi-chloride which was recrystallized from benzene petroleum ether (b.p.60-80°) (2.98 g; 83%), m.p. 142° [lit.10 m.p. 143°].

The oxidative addition reactions of Ar₃M compounds [M = As, Sb; Ar = Ph or p-tol.] with M'X₂ (M' = Cu(II), Hg(II); X = Cl, Br, I, NCS, CH₃COO) provided a simple and direct route for the synthesis of Ar₃M₃X derivatives (Eq. 1). The products were obtained in good yield (70 to 85%) without any contamination, since M₃X₄ were easily separated due to their very low solubility.

Ar₃M + 2M'X₂ ➞ Ar₃M₃X₂ + M₄X₄ . . . (1)

The formation of cupric or mercuric salts (Ar₃Mₓ) or of diaryl-arsenic or -antimony (Ar₂MX), expected from the possible aryl-metal bond cleavage, was not observed. No trace of aryl-halides (ArX) and aryl-cupric or-mercuric salts was observed even in the presence of excess of M'X₂. The method is, therefore, very suitable for the synthesis of Ar₃MX₄. The method is also advantageous over literature methods for preparing triarymetal diiodides which are generally more difficult to obtain in the pure state and is of particular interest for the preparation of triaryl-arsenic and —antimony diacetates which

<table>
<thead>
<tr>
<th>Ar₃M M’X₂</th>
<th>M’X₂</th>
<th>Products</th>
<th>m.p. (°C) (lit. m.p.)</th>
</tr>
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<tbody>
<tr>
<td>Ph</td>
<td>As Cl</td>
<td>Ph₃AsCl₂</td>
<td>204(205)°</td>
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<tr>
<td>p-Tolyl</td>
<td>As Cl</td>
<td>(p-Tolyl)₃AsCl₂</td>
<td>220(230)°</td>
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<tr>
<td>Ph</td>
<td>As Br</td>
<td>Ph₃AsBr₂</td>
<td>213(215)°</td>
</tr>
<tr>
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<td>(p-Tolyl)₃AsBr₂</td>
<td>214(216)°</td>
</tr>
<tr>
<td>Ph</td>
<td>Sb Br</td>
<td>Ph₂SbBr₄</td>
<td>244(245)°</td>
</tr>
<tr>
<td>p-Tolyl</td>
<td>Sb Br</td>
<td>(p-Tolyl)₂SbBr₄</td>
<td>232(234)°</td>
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<tr>
<td>Ph</td>
<td>Sb I</td>
<td>Ph₂SbI₂</td>
<td>138(140)°</td>
</tr>
<tr>
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<td>150(153)°</td>
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<tr>
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<td>170(172)°</td>
</tr>
<tr>
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<td>As Cl</td>
<td>Ph₃AsCl₂</td>
<td>181(183)°</td>
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<tr>
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<td>As Cl</td>
<td>(p-Tolyl)₃AsCl₂</td>
<td>210</td>
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<tr>
<td>Ph</td>
<td>As CO₂</td>
<td>Ph₃As(CO₂)₂</td>
<td>248</td>
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<tr>
<td>p-Tolyl</td>
<td>As CO₂</td>
<td>(p-Tolyl)₃As(CO₂)₂</td>
<td>225</td>
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<tr>
<td>Ph</td>
<td>Sb CO₂</td>
<td>Ph₂Sb(CO₂)₂</td>
<td>108(110)°</td>
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<tr>
<td>p-Tolyl</td>
<td>Sb CO₂</td>
<td>(p-Tolyl)₂Sb(CO₂)₂</td>
<td>104(105)°</td>
</tr>
<tr>
<td>Ph</td>
<td>SCN</td>
<td>Ph₃Sb(SCN)₃</td>
<td>160(162)°</td>
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<tr>
<td>p-Tolyl</td>
<td>SCN</td>
<td>(p-Tolyl)₃Sb(SCN)₃</td>
<td>148°</td>
</tr>
</tbody>
</table>

*Compounds gave satisfactory elemental analyses.

NOTES

10. BLYHOLDER, G., Proceedings third international Congress on Catalysis (North Holland, Amsterdam), I (1965), 657.

TABLE 1 - REACTIONS OF TRIARYL-ARSINES AND -STIBINES WITH METALLIC SALTS (M'X₂)
are mostly obtained in low yields by metathetical reactions.

The νas NCS in the IR spectra of Ar₂M(NCS)₃ compounds is observed in the region 2010 ± 20 cm⁻¹ in good agreement with those reported² for Pb₂M(NCS)₃. The IR spectra of Ar₂M(OCOC₂H₅) νCO at 1625 ± 10 cm⁻¹ consistent with five coordinated structure containing unidentate carboxylate group, similar to those reported² for Pb₂SB(OCOC₂H₅)₂.

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References

Behaviour of Some Sulphur-Nitrogen Compounds in Disulphuric, Chlorosulphuric & Fluorosulphuric Acids

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Conductance behaviour of thiotriiazyl chloride and bromide and some of their adducts has been studied in disulphuric, chlorosulphuric and fluorosulphuric acid media.

An improvement in the method of preparation of thiotriiazyl chloride³ has increased interest in the chemistry of this unusual cation. It is, therefore, of some interest to investigate its behaviour in halosulphuric acids and also to see the stability of the N-S ring system in highly acidic and oxidizing solvents.

Thiotriiazyl chloride was prepared by the method reported by Jolly et al.⁴. Thiotriiazyl bromide was obtained by dissolving S₄N₃Cl in anhydrous formic acid and reacting it with solid potassium bromide⁵ when the bromide salt was precipitated. The adduct S₄N₃SbCl₄ was obtained by mixing S₄N₃Cl and SbCl₅ in anhydrous formic acid in their stoichiometric ratios. The adducts S₄N₃TeBr₄, (S₄N₃)₂TeBr₆ and S₄N₃SbBr₄ were also prepared by mixing the reactants in their stoichiometric ratios in anhydrous methylene chloride for a few hours. The solvents like H₂SO₄, HSO₃F and HSO₃Cl were prepared and purified by the methods already reported in literature⁶-⁹.

Thiotriiazyl bromide dissolves quickly in disulphuric and chlorosulphuric acids, whereas compounds of the type S₄N₃TeBr₄, (S₄N₃)₂TeBr₆, S₄N₃SbCl₄ and S₄N₃SbBr₄ dissolve slowly in these solvents. The conductances of these solutions do not change with time which suggests that there is no decomposition of the compounds in disulphuric and chlorosulphuric acids. UV spectra of the solutions of S₄N₃Br in disulphuric and chlorosulphuric acids show bands at 240 and 320 nm which further confirm the presence of thiotriiazyl cation in both these acids. The spectrum is identical to that of the solution of thiotriiazyl chloride in other strong acids⁶-⁷. However the conductance data (Fig. 1) suggest the following modes (Eqs 1-10) of reactions in both these solvents, and support the presence of ionizable bromide ion. These findings are in good agreement with those of Paul and co-workers, where ionic complexes have been prepared with Lewis acids.

\[
\begin{align*}
2S₄NaBr + 6H₂SO₄ & \rightarrow 2S₄N₃+ + 2HSO₄⁻ + Br₂ + 5H₂SO₄ + SO₂ (1) \\
S₄NaBr + 4HSO₃Cl & \rightarrow 2S₄N₃+ + 2SO₂Cl⁻ + H₂SO₄ + Br₂ + 2HCl + SO₂ (2) \\
S₄NaBr + 2S₂O₇²⁻ & \rightarrow 2S₄N₃+ + Sb(HS₃O₃)₃+ + 2H₂SO₄ + 2H₂SO₃ (3) \\
S₄NaBr + 12HSO₄⁻ & \rightarrow 2S₄N₃+ + 10H₂SO₄ + 2Br₂ + 2SO₂ (4) \\
S₄NaBr + 4HSO₃Cl & \rightarrow 2S₄N₃+ + TeBr₄⁺ + 2SO₂Cl⁻ + 2H₂SO₄ + Br₂ + 3SO₂ (5) \\
2(S₄Na₃)₂TeBr₆ + 18H₂SO₄ & \rightarrow 4S₄N₃+ + 2TeBr₄⁺ + 6H₂SO₄ + 3Br₂ + 3SO₂ (6) \\
S₄NaSbBr₄ + 8HSO₃Cl & \rightarrow S₄N₃+ + Sb(HSO₄)₃ + 4HSO₄⁻ + 4HCl (7) \\
S₄NaSbCl₄ + 12H₂SO₄ & \rightarrow S₄N₃+ + Sb(HSO₄)₂ + 10H₂SO₄ + 2Br₂ + 2SO₂ (8) \\
S₄NaSbCl₄ + 4HSO₃Cl & \rightarrow S₄N₃⁺ + TeBr₄⁺ + 2SO₂Cl⁻ + 2H₂SO₄ + Br₂ + H₂SO₄ + SO₂ (9) \\
2(S₄Na₃)₂TeBr₆ + 12HSO₃Cl & \rightarrow 4(S₄N₃)+ + 2TeBr₄⁺ + 6SO₂Cl⁻ + HCl + 3Br₂ + 2H₂SO₄ + 3SO₂ (10)
\end{align*}
\]

The formation of cations of the type TeBr₄⁺ has already been reported in these strong acids⁶-¹⁰. The presence of sulphur dioxide in the above reactions has further been confirmed by taking the UV spectra of the solutions which show the absorption band at 280 nm (ε₄ₙ = 1050). Sulphur dioxide and bromine produced in the above reactions behave as non-electrolytes¹¹-¹² in both these solvent acids, whereas, H₂SO₄ and HCl behave as weak bases in chlorosulphuric acid¹³-¹⁴.