Inorganic Syntheses, Volume XI
Edited by William L. Jolly

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37. TRIALKOXYARSINES

(*Trialkyl Arsenites*)

$$\mathrm{AsCl_3 + 3ROH + 3NR'_3 \rightarrow As(OR)_3 + 3R'_3NHCl}$$

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Trimethoxyarsine was first reported by Crafts.[1] It was obtained by three methods: from silver arsenite and methyl iodide, from arsenic trioxide and tetramethoxysilane, and from arsenic trihalide and sodium methoxide. Better yields have been obtained by applying the method of this synthesis; the procedure seems to be generally applicable to the preparation of trialkoxyarsines.

■ ***Caution.*** *Although the toxicity of trialkoxyarsines has not been investigated in detail, precautions similar to those suggested for the handling of volatile arsenic compounds should be taken. Therefore these preparations should be performed in a well-venti-*

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lated hood, and contact of the arsenic-containing solutions with the skin should be avoided.

Procedures

A. TRIMETHOXYARSINE

(Trimethyl Arsenite)

A four-necked 3-l. flask fitted with a thermometer, reflux condenser, dropping funnel, and mechanical stirrer is charged with 750 ml. of *n*-hexane, 750 ml. of anhydrous ethyl ether, 104 g. (3.25 moles) of anhydrous methanol, and 370 g. (3.05 moles) of *N*,*N*-dimethylaniline.* A drying tube is attached to the outlet of the condenser to prevent moisture from entering the reaction vessel. The dropping funnel is charged with 182 g. (1 mole) of freshly distilled arsenic trichloride,† and this is added drop by drop to the well-stirred ice-cooled contents of the reaction flask. The temperature in the flask is maintained at *ca.* +5°. During the course of the addition, a white precipitate of *N*,*N*-dimethylaniline hydrochloride is formed.

When the addition of the arsenic trichloride is completed, the reaction mixture is stirred for another 1 to 2 hours at room temperature. The solution is filtered with careful exclusion of the moisture of the atmosphere,‡ and the *N*,*N*-dimethylaniline hydrochloride precipitate is washed with cold ethyl ether. The combined filtrates are distilled using a 60-cm. vacuum-jacketed column filled with glass helices.§ The trimethoxyarsine distills at 129–130°/760 mm.; yield 129 g. (77%). Yields of 118–126 g. are obtained using triethylamine.

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* Triethylamine (308 g.) may be used, but then a smoke and a crusty deposit of Et_3NHCl form during the addition of the $AsCl_3$. The bulk of the Et_3NHCl precipitate is very voluminous and at times is difficult to filter. The use of *N*,*N*-dimethylaniline (suggested by the checkers) avoids these problems.

† The checkers successfully used freshly opened bottles of analytical reagent grade $AsCl_3$ without further purification.

‡ The checkers used a dry-nitrogen-filled plastic glove bag.

§ The checkers used a 1-m. vacuum-jacketed Oldershaw column, with a 2:1 reflux ratio.

B. TRIETHOXYARSINE

(Triethyl Arsenite)

The same method, but using 148 g. (3.25 moles) of anhydrous ethanol instead of methanol in the procedure given above, may be utilized to prepare triethoxyarsine; yield 148 g. (70.5%); b.p. 59°/14 mm. or 167°/760 mm. Yields of 135–145 g. are obtained using triethylamine.

C. TRI-*n*-BUTOXYARSINE

(Tri-*n*-butyl Arsenite)

Tri-*n*-butoxyarsine may be prepared according to the procedure given above by using 240 g. (3.25 moles) of dried 1-butanol instead of the methanol and 308 g. (3.05 moles) of triethylamine instead of the *N*,*N*-dimethylaniline. Yield: 244 g. (83%); b.p. 101°/3 mm. The checkers used *N*,*N*-dimethylaniline and obtained a yield of 192 g. (66%), b.p. 102°/4 mm.

Properties[2]

Trimethoxyarsine (d_0^{20} 1.4264; n_D^{20} 1.4402) is a colorless liquid which is readily hydrolyzed by atmospheric moisture, forming a white precipitate of arsenic trioxide. The compound is soluble in carbon tetrachloride, benzene, chloroform, hydrocarbons, and ethers. The product is shown to be at least 99.5% pure (with respect to hydrogen-containing impurities) by proton nuclear magnetic resonance (n.m.r.), since a single sharp peak at −3.52 p.p.m. (relative to internal tetramethylsilane) is seen in the n.m.r. spectrum of the neat liquid. Similar properties are shown by triethoxyarsine (d_0^{20} 1.2132; n_D^{20} 1.4360) and tri-*n*-butoxyarsine (d_0^{20} 1.0723; n_0^{20} 1.4476).

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