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Preliminary communication

ACTIVATED METALS

VI*. PREPARATION AND REACTIONS OF HIGHLY REACTIVE INDIUM METAL

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Summary

Highly reactive indium powder, prepared by alkali metal reduction of indium salts in hydrocarbon solvents, reacts at moderate temperatures in hydrocarbon solvents with alkyl iodides to give dialkylindium iodides, and with iodine to give indium monoiodide.

We recently reported procedures for the preparation of highly reactive magnesium [2], zinc [3], and aluminum [1] powders. We now describe a procedure for the preparation of highly reactive indium powder and the reaction of this indium powder with alkyl iodides and with iodine.

The usual procedure for the preparation of the highly reactive indium powder is the reduction of anhydrous indium trichloride with alkali metals in hydrocarbon solvents under an argon atmosphere. The boiling point of the solvent should exceed the melting point of the alkali metal.

Little work has been reported concerning the direct synthesis of alkylindium halides. Recently, Gynane and coworkers [4] reported the direct reaction of indium metal with alkyl halides, involving reaction times, of a day or more, and the product was a mixture of R_2InX and $RInX_2$. We have found that our indium will react with methyl and ethyl iodide in 2 h at 80° in xylene to give nearly quantitative yields of a single product, the dialkylindium iodide. The overall reaction scheme is

$$InCl_3 + 3M \rightarrow In^{\star} + 3MCl \qquad (M = K \text{ or } Na)$$
$$2In^{\star} + 2RI \rightarrow R_2InI + InI$$

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[*] For part V of series see ref. 1.

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Under our conditions the indium monoiodide does not react further with additional alkyl iodide as has been reported [5, 6]. Additional reactions were attempted with indium monoiodide and alkyl iodides in the presence of alkali salts under our reaction conditions, but no reaction was observed.

Further evidence of the high reactivity of the indium powder comes from its reaction with iodine. The standard method for the preparation of indium monoiodide involves the heating of stoichiometric amounts of indium metal and iodine at 400°C for 24 h [6]. We find that iodine reacts with the activated indium powder in refluxing xylene quantitatively in 30 minutes and the indium monoiodide formed is easily separated and purified.

The activated indium powder was prepared in the following manner. Anhydrous $InCl_3$ (Alfa ultrapure, 20 mmoles) was placed in a flask with a side arm equipped with a septum cap in a dry box. Freshly distilled xylene 25 ml was added, followed by adding freshly cut potassium (2.34 g, 60 mmoles). The mixture was heated to reflux and stirred with a magnetic stirrer under argon. The reduction was generally complete in 4 to 6 h, yielding a light black powder. The alkyl iodide (30 mmole, R = Me, Et) in 50% excess and internal standard were added, and the mixture kept at 80°. Aliquots were periodically quenched in 10% HCl solution, and the % of reaction was determined by measuring the disappearance of alkyl iodide. The reactions of methyl iodide and ethyl iodide with activated indium reached 100 and 97% after 2 h, respectively*.

Dimethylindium iodide was obtained by either crystallization from xylene or sublimation under reduced pressure. The IR spectrum** showed C—In stretching frequencies at 552s and 478w cm^{-1} (lit. [7], 548s, 480w cm^{-1}) and mass spectrum showed molecular ion *m/e* 272. Diethylindium iodide was also obtained by sublimation, m.p. 171—174° (lit. [8], 171—173°C). The IR spectrum showed C—In stretching frequencies at 450s and 505s cm^{-1} (lit. [8], 455, 506 cm^{-1}) and mass spectrum showed molecular ion *m/e* 300.

Sublimed iodine (1.27 g, 5 mmoles) was added to activated indium (prepared from 2.21 g of $InCl_3$ and 1.17 g of potassium) in xylene (25 ml). After refluxing for 30 minutes, the reaction was complete. The red indium monoiodide was collected by filtration, washed with water to remove the alkali salts and dried under reduced pressure. The product analysed correctly for InI (Calcd.: In, 47.50; Found: In 46.80, 47.91) the indium was determined by EDTA titration using 4-(2-pyridylazo)resorcinol as indicator or atomic absorption spectroscopy.

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*The % of reaction was determined by measuring the disappearance of alkyl iodide comparing with internal standard by G.C. after aliquots having been quenched.

**The spectrum was recorded by interferometer (FTS 14, Infrared Spectrophotometer).

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