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Preliminary communication

The synthesis of lower alkylindium halides by the direct reaction between the metal and alkyl halides

M.J.S. GYNANE, L.G. WATERWORTH and I.J. WORRALL
Department of Chemistry, The University, Lancaster (Great Britain)

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SUMMARY

Metallic indium reacts directly with the alkyl halides RX (R = Me, Et, n-Pr; X = Br, I) to give the mixed products $RInX_2$ and R_2InX.

In view of the similarities between aluminium and indium, indium metal might be expected to undergo direct reaction with organic halides. Schumb and Crane[1] have reported that reactions between several organic halides and metallic indium, including lower alkyl halides were unsuccessful but found that a very slow reaction occurred between indium metal and mehylene diiodide. Although they were unable to isolate a product, they concluded that indium–carbon bonds had been formed and suggested that ICH_2InI_2 might have been present in the products. The only successful metal/organic halide reaction reported is that between C_6F_5I and indium metal[7]. We have now found that reactions between metallic indium and lower alkyl bromides and iodides readily occur to give mixtures of alkylindium dihalides and dialkylindium monohalides.

About ½g of metallic indium (99.999%) was shaken at room temperature with excess alkyl halide RX (R = Me, Et, n-Pr; X = Br, I), *in vacuo*. For the iodide series light was excluded in order to prevent photo-decomposition of alkyl iodide. The iodide reactions were more rapid and were complete in 1–3 days; the bromide reactions took between 3–5 days. After removal of the excess alkyl halide, white crystalline products were obtained for all the reactions apart from that between n-propyl iodide and indium metal which produced a colourless, viscous liquid. The products analysed as $R_3In_2X_3$ and their Raman spectra in the In–C region are given in Table 1 together with those of the alkylindium dihalides and dialkylindium monohalides (where known).

These results suggest that for the methyl and ethyl systems the following reactions occur:

$$2\text{In} + 3\text{RX} \longrightarrow \text{R}_2\text{InX} + \text{RInX}_2.$$

For the n-propyl iodide reaction the spectra are not so readily interpreted since there are no spectroscopic data known for di-n-propylindium monoiodide. Further even for n-propylindium diiodide two strong broad bands are observed which we have previously assigned to the indium—carbon stretching frequencies of the *trans* and *gauche* forms similar to those observed in $Sn(n\text{-}Pr)_4$[6]. However the extra broad band in the product spectrum coupled with the analytical data support the conclusion that both mono- and di-n-propylindium iodides are formed in the reaction. For the n-propyl bromide reaction satisfactory Raman spectra could not be obtained because of sample fluorescence, but again analytical data supports mixed compound formation.

TABLE 1

ν(In–C) FREQUENCIES (cm^{-1})

Reaction	*Product*	*$RInX_2$*	*Reference*	*R_2InX*	*Reference*
In/MeBr	523s, 486s, 559vw	523s	2	554s, 486w[a]	3
In/EtBr	494s, 460s	494s	5	460, 512[a]	4
In/MeI	486s, 509s, 555vw	512s	5	548s, 480vw[a]	3
In/EtI	486s, 455s	489s	5	455, 506[a]	4
In/n-PrI	488s (br), 561s (br) 575 (br)	486s (br) 576s (br)	5		

[a] IR

The potential of these reactions with respect to the preparation of organoindium compounds and use in organic synthesis is under investigation.

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