CCLIII.—*Methylmercuric Halides and Hydroxide.*

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AN attempt to repeat Marvel and Gould's preparation of methylmercuric iodide by the action of magnesium methyl iodide upon an excess of mercuric chloride suspended in ether (*J. Amer. Chem. Soc.*, 1922, **44**, 153) resulted only in the production of the double compound $CH_3{\cdot}HgCl,2CH_3{\cdot}HgI$ and a small quantity of methylmercuric chloride. If the Grignard reagent was added very slowly to the suspension of mercuric chloride, a copious precipitate of mercuric iodide soon formed, which readily dissolved on further addition of the reagent. The formation of mercuric iodide can be explained by assuming that the methylmercuric iodide produced by reaction (1) reacts with the excess of mercuric chloride in accordance with equation (2).

$$CH_3{\cdot}MgI + HgCl_2 = CH_3{\cdot}HgI + MgCl_2 \quad . \quad . \quad . \quad (1)$$

$$2CH_3{\cdot}HgI + HgCl_2 = 2CH_3{\cdot}HgCl + HgI_2 . \quad . \quad . \quad (2)$$

In support of this assumption, it was found that the latter reaction occurs readily in alcoholic or ethereal solution. The subsequent solution of mercuric iodide on further addition of the Grignard reagent is explained by their interaction as represented by the equation (3).

$$CH_3{\cdot}MgI + HgI_2 = CH_3{\cdot}HgI + MgI_2 \quad . \quad . \quad . \quad (3)$$

This reaction proceeds smoothly and serves as a convenient method for the preparation of methylmercuric iodide in quantity. The fact that the double compound $CH_3{\cdot}HgCl,2CH_3{\cdot}HgI$ was obtained instead of methylmercuric iodide in the repetition of Marvel and Gould's experiment adds further support to the above assumption, since it was observed that from a hot alcoholic solution of methylmercuric chloride and iodide the stable double compound crystallised on cooling. The double compound is converted by mercuric chloride into methylmercuric chloride, and it is probable that the small amount of the latter which was found associated with the double compound in the original reaction product owed its origin to this cause, since the amount formed increased with the excess of mercuric chloride originally employed. From a consideration of these facts, it would appear impossible to obtain methylmercuric iodide under the conditions of Marvel and Gould.

Methylmercuric hydroxide has long been known in solution (Frankland, *Annalen*, 1853, **85**, 368; Dunhaupt, *ibid.*, 1854, **92**, 381; *J. pr. Chem.*, 1854, **61**, 399; Crymble, J., 1914, **105**, 666), but it was first isolated in the solid form by Sneed and Maynard (*J. Amer. Chem. Soc.*, 1922, **44**, 2946) from methylmercuric iodide and moist silver oxide in the presence of a small amount of alcohol.

Sneed and Maynard's method of purification of the base—precipitation from saturated alcoholic solution with a large excess of dry ether—is very wasteful, for large quantities of ether are necessary, the base undergoes much decomposition in its presence, and five repetitions of the process do not effect complete purification (m. p. 104°). A method is now described whereby the purification can be efficiently and rapidly achieved without loss of material. The pure base so obtained differs from that prepared by Sneed and Maynard both in melting point and in solubility.

EXPERIMENTAL.

Action of Magnesium Methyl Iodide on Mercuric Chloride.—The Grignard reagent prepared from 2·4 g. of magnesium was added to 30 g. of finely powdered mercuric chloride suspended in 250 c.c. of dry ether under the conditions described by Marvel and Gould (*loc. cit.*). The crude product was crystallised from hot thiophen-free benzene and then fractionally from methyl alcohol, the less soluble mercuric iodide and methylmercuric chloride being thereby removed; the final product was obtained in small, pearly leaflets, m. p. 129°

(Found : Cl, 4·0; I, 27·1. $C_3H_9ClI_2Hg_3$ requires Cl, 3·8; I, 27·0%). The double compound differs from methylmercuric chloride in having a much more intense and unpleasant odour.

Methylmercuric iodide was prepared under the conditions previously described, mercuric chloride being replaced by the equivalent amount of mercuric iodide. The product crystallised from methyl alcohol in transparent, rectangular plates melting at 145° and not 143° as stated in the literature (Found : I, 36·9. Calc. : I, 37·05%).

Methylmercuric Hydroxide.—Methylmercuric iodide (10 g.) in 50 c.c. of methyl alcohol and 2 c.c. of water was mechanically agitated for 3 hours with 7 g. of moist silver oxide containing 34% of water. The filtered solution was evaporated to dryness in a vacuum at 40°, the white residue warmed to 30° with 20 c.c. of chlorobenzene, in which it was very sparingly soluble, and alcohol added until solution was just effected, the temperature being kept at 30°; the alcohol was then removed in a vacuum over sulphuric acid, and the base, which separated in small crystals, was drained from the chlorobenzene and washed with light petroleum (previously treated with alcoholic potassium hydroxide to remove sulphur compounds, since these react readily with methylmercuric hydroxide). This process of purification was repeated several times; the base then obtained, after drying in a vacuum, melted at 106° (Found, by Rupp and Nöll's method, Meyer's "Lehrbuch der Organisch-Chemischen Methodik," 1922, p. 359 : Hg, 86·0. Calc. for CH_4OHg : Hg, 86·2%). The pure base forms white crystals with a pearly lustre having a faint, unpleasant odour. It decomposes slowly on standing, more rapidly in presence of ether. When heated above its melting point, it partly decomposes and then detonates violently. Contrary to the statements of Sneed and Maynard, it is very sparingly soluble in cold benzene, toluene, carbon tetrachloride, and light petroleum.

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