Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

SHORT COMMUNICATION

An improved preparation of dialkylzinc compounds

The standard method[1] for the preparation of dialkylzinc compounds is through the reaction of the alkyl iodide, or a mixture of iodide and bromide, with a zinc/copper couple, prepared by reducing copper oxide with hydrogen in the presence of zinc or by alloying the molten metals. Subsequent workers have reported the preparation of the couple from zinc dust and copper citrate[2] or the use of high boiling ethers as solvent[3].

In all the above work, the preparation and condition of the metal mixture appears to be critical, and in consequence these methods are not suitable for the casual preparation of small quantities of dialkylzinc compounds. We now report a modification of the above preparation by means of which dimethylzinc and diethylzinc may be easily prepared from readily available materials.

We find that reaction of methyl iodide with zinc occurs readily at 110° in a sealed tube in the presence of copper. Under these conditions, no elaborate preparation or pre-conditioning of the zinc/copper mixture is necessary; the two metal powders are simply mixed by shaking. The conversion of methyl iodide to dimethylzinc is reproducibly high (80–90%) and the volatile product may readily be handled and purified by standard vacuum techniques, thus avoiding contamination by contact with the atmosphere. The method has been successfully used for quantities up to 4 g of dimethylzinc. While we feel that this is quite safe in glass apparatus (provided standard precautions are taken when dealing with volatile materials), we suggest that any substantially larger scale of preparation should be either divided between several reaction tubes or carried out in a pressure vessel.

The analogous reaction using ethyl iodide proceeds readily, but at a slower rate, giving diethylzinc of high purity.

Experimental

In a typical preparation, zinc dust (6.0 g, B.D.H. 'Analar' grade) and copper metal (1.5 g, Fisher electrolytic dust) were mixed in a Pyrex Carius tube (50 ml). After evacuating and cooling the tube, methyl iodide (9.2 g, Columbia Organic Chemicals Co.) was condensed on and the tube sealed. After keeping at 110° for 5 hours, the tube was opened to the vacuum system and volatile products removed. Fractional condensation through traps cooled to −46°, −78° and −196° gave dimethylzinc, condensing at −78° (2.5 g, 80%) and a small quantity of hydrocarbon material (mainly ethane) condensing at −196°. In several preparations the yield of dimethylzinc varied between 80 and 95%, but unreacted methyl iodide was never found. The purity of the dimethylzinc was checked by molecular weight determination (gas density, found 95, calcd. 95) and infrared spectroscopic examination.

With ethyl iodide (B.D.H.) the reaction proceeded similarly. After keeping at 100° for 5 hours, fractional condensation gave diethylzinc, condensing at −36°, in 65% yield based on ethyl iodide reacting (62%), and unchanged ethyl iodide, condensing at −78°. Only a trace of hydrocarbon was produced under these conditions, but at higher temperatures (135°) considerable decomposition to hydrocarbon was evident and the yield of diethylzinc was much reduced.

Acknowledgement

We gratefully acknowledge financial support from the National Research Council of Canada.

Chemistry Department,
University of Western Ontario,
London (Canada)

N. K. Hota
C. J. Willis

1 C. R. Noller, *Org. Syn., Collective Vol.*, 2 (1943) 384.
2 R. C. Krug and P. J. C. Tang, *J. Am. Chem. Soc.*, 76 (1954) 2262.
3 L. F. Hatch, G. Sutherland and W. J. Ross, *J. Org. Chem.*, 14 (1949) 1130.

Received December 19th, 1966