Activated Metals. Preparation of Highly Reactive Zinc[1]

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Summary A method of preparing highly reactive zinc powder is presented; this zinc powder has been shown to react directly with alkyl and aryl bromides.

WE report here on a new procedure for the preparation of finely divided zinc powder and some of the chemical reactions this very reactive powder undergoes. Although zinc[2] and zinc–copper couples[3,4] have been reported to react with alkyl iodides, there have been few reports of zinc–copper couples reacting with alkyl bromides[4] and no reports of reaction with aryl bromides.

We have prepared zinc metal in a finely divided state which appears to be much more reactive towards alkyl and aryl halides than any previously described in the literature. Among the reactions we have carried out in high yields are the direct reaction of bromobenzene and alkyl bromides with the zinc powder.

The activated zinc powder is prepared in the following manner. Anhydrous zinc bromide (13·06 g, 0·058 mol) which had been dried under vacuum at 150° overnight was dissolved in 40 ml of dry THF. Potassium (4·52 g) was then added and the resulting mixture heated under reflux for 4 h. The solvent was removed under vacuum leaving a dark grey powder. Bromobenzene (7·75 g, 0·0493 mol) and diglyme (20 ml) were added to the zinc powder and the resulting mixture was heated under reflux for 8 h. Removal of the diglyme at 130° under vacuum yielded a black residue. Acid hydrolysis of the residue gave benzene (3·18 g, 0·0407 mol) in 83% yield by g.c. analysis. In additional experiments, the phenylzinc bromide was found to react with benzaldehyde, propionaldehyde, and n-butyraldehyde to give the corresponding alcohols which were identified by n.m.r. and i.r.

The use of diglyme in the preparation of the phenylzinc bromide is necessary as the reaction does not proceed in glyme under reflux.

n-Butyl bromide (5·48 g, 0·041 mol) was treated with the activated zinc (prepared from 4·76 g of potassium and 13·73 g of zinc bromide) in dimethoxyethane (40 ml) for 3 h under reflux. The black precipitate of zinc powder disappeared during this time. The solvent was removed and a bulb-to-bulb distillation at 100° under vacuum yielded di-n-butylzinc (3·42 g, 0·0194 mol) in 97% yield based on n-butyl bromide used. The di-n-butylzinc was identified by n.m.r. [τ 9·75 (4H, t), 9·14 (6H, m), and 8·2–9·0 (8H, m)].

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