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Preliminary communication

The reaction of diborane with Grignard reagents: a new route to organoboranes, phenols and alcohols

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A recent communication[1] reported the formation of organoboranes from arylmercury compounds by reaction with borane in tetrahydrofuran. Under the same conditions alkylmercury compounds did not give organoboranes in significant yields. The use of Grignard reagents, however, proved more successful, and several alkyl halides were thus converted into organoboranes which, without isolation, were oxidised with alkaline hydrogen peroxide to the corresponding alcohols in yields of 40–60%. In a number of instances a Wurtz type side reaction[2] accompanied formation of the Grignard reagent, the bialkyl being formed before the reaction with borane could take place. To minimise this side reaction a modified experimental procedure has now been developed in which the

TABLE 1

Substrate	Product	Yield [a] (%)
Bromobenzene	Phenol	67
p-Bromotoluene	*p*-Cresol	76
m-Bromotoluene	*m*-Cresol	65
p-Methoxybromobenzene	*p*-Methoxyphenol	61
m-Methoxybromobenzene	*m*-Methoxyphenol	74
m-Chloroiodobenzene	*m*-Chlorophenol	77
9-Bromophenanthrene	9-Hydroxyphenanthrene	62
1-Bromobutane	n-Butanol	73
2-Bromobutane	sec-Butanol	59
	n-Butanol [b]	3
1-Bromooctane	n-Octanol	82
2-Bromooctane	2-Octanol	59
	1-Octanol [b]	13
1-Bromohexadecane	1-Hexadecanol	95
Benzyl bromide	Benzyl alcohol	99
Cyclohexyl bromide	Cyclohexanol	67
Cyclopentyl bromide	Cyclopentanol	60
1-Bromoadamantane	1-Hydroxyadamantane	48

[a] The yields of phenols were determined by UV, the yields of alcohols were determined by GLC, 1-hydroxyadamantane was isolated.
[b] Formed by isomerisation of the organoborane.

Grignard reagent is formed in the presence of BH_3, and so converted at once into the organoborane. The standard reaction conditions involve reaction of 10 millimoles of halide with 10 milliatoms magnesium and 15 millimoles BH_3, in refluxing tetrahydrofuran. The reaction is essentially complete after 45 minutes and the work-up follows normal hydroboration–oxidation procedures[3]. The method is applicable to both aromatic and aliphatic (including bridgehead) halides. Typical results are shown in Table 1.

The scope of the method appears to be governed by the efficiency of Grignard reagent formation, and once formed, the organomagnesium compound can be converted essentially quantitatively into the organoborane. This was shown in experiments in which Grignard reagents were prepared and divided in two. One half was treated with water to form a hydrocarbon, the other half was treated with borane to form the organoborane and eventually, the alcohol. The yields of alcohol and hydrocarbon were the same within experimental error.

Grignard reagents have been used before[4] for the preparation of organoboranes by treatment with boron halides or alkoxides, which generally leads to trialkyl boranes or boronic and borinic acids. Trimethoxyboron has been used in the conversion of aryl halides to phenols via Grignard reagents and organoboron compounds but the yields were varied[5]. We consider that the use of borane offers a significant advantage both in the mildness of the experimental procedure and in the excellent yields obtainable. This reaction offers not only a simple and convenient method for the replacement of halides by hydroxyl in both aliphatic and aromatic compounds, but also a new route to organoboranes not accessible via direct hydroboration.

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