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Preliminary communication

REACTIONS OF ORGANOMETALLIC COMPOUNDS WITH DIBORANE

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Summary

Phenols are obtained in good yields by hydrogen peroxide oxidation of the products formed from aryl halides and diborane in the presence of Li, K, or Ca in THF.

The reactions of diborane with organometallic compounds have received comparatively little attention. Some early studies were carried out by Schlesinger and Brown [1], who found that ethyllithium and the methyl derivatives of aluminium and gallium reacted with diborane to give metal borohydrides, and Holliday and Jessop [2] have reported the formation of alkylborons from tetramethyl- and tetravinyl-lead and diborane. However, the synthetic uses of reactions of this type have been examined only very recently, when the synthesis of phenols from the hydroborations of organomercury compounds [3] and Grignard reagents [4], and the preparation of 1,3-diols from allylic lithium reagents [5] were reported.

We wish to report some preliminary studies of the reactions between diborane and the organic derivatives of lithium, potassium, and calcium, and the further reaction of the intermediates so formed with alkaline hydrogen peroxide solution, to yield phenols as the final products. The organometallic compounds were not prepared in a separate stage, but were generated in situ in the presence of a two-fold excess of diborane in THF as solvent, thus simplifying the overall synthetic procedure*. In a typical reaction using lithium, freshly cut pieces of the metal were placed in a flask containing a one molar solution of diborane, and the organic halide was added over a period of fifteen minutes. The mixture was stirred for two hours at room temperature, and then treated with alkaline hydrogen peroxide solution, using normal hydroboration-oxidation procedures [7]. A similar procedure was used in three experiments using calcium or potassium,

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*A recent report [6] shows that one-stage reactions in which organolithium compounds are generated in the presence of carbonyl compounds give the expected products in appreciably higher yields than the conventional two-stage reactions.

TABLE 1

YIELDS OF PHENOL OBTAINED BY OXIDISING THE PRODUCTS OBTAINED FROM REACTIONS OF *ORGANIC HALIDES* WITH DIBORANE AND A METAL IN THF

Halide	Metal	Yield (%) of ArOH
Chlorobenzene	Li	80
Bromobenzene	Li	66
Iodobenzene	Li	52
m-Chlorotoluene	Li	60
m-Bromotoluene	Li	51
o-Bromotoluene	Li	68
p-Bromotoluene	Li	53
p-Chloroanisole	Li	52
p-Bromoanisole	Li	42
o-Bromoethylbenzene	Li	34
p-Bromoethylbenzene	Li	68
2-Bromomesitylene	Li	77
p-Bromophenetole	Li	52
Bromobenzene	K	45
m-Bromotoluene	K	23
o-Bromotoluene	K	25
Bromobenzene	Ca	8
Iodobenzene	Ca	48
m-Iodotoluene	Ca	36
p-Iodotoluene	Ca	34
p-Iodoanisole	Ca	28

except that the initial addition was carried out at —15°, and the reaction mixture was left at room temperature for 48 h before oxidation. The yields of phenols were determined quantitatively by GLC and UV, and in some reactions the product was isolated. The results are shown in Table 1.

It can be seen that for the systems using lithium, phenols can be obtained in high yields under mild conditions and a large excess of diborane is not required. Considerably lower yields are obtained when potassium or calcium are used, and for calcium systems only the organic iodides give significant yields. However, the potassium systems are of some interest in that they show the value of one-stage reactions for highly reactive organometallic compounds. The superiority of the one-step method using lithium was also demonstrated by carrying out reactions under analogous conditions, but using preformed organolithium compounds, when considerably lower yields of phenols were obtained. For example, preformed phenyllithium and *m*-tolyllithium gave yields of 9 and 45% respectively, whereas the one-stage processes gave yields of 66 and 60% (see Table 1).

So far in these investigations, no attempt has been made to isolate the reaction intermediates, but the most probably reaction sequence is indicated:

$$\mathrm{ArX} + \mathrm{M} \xrightarrow{B_2H_6} (\mathrm{Ar{-}B}\!<) \xrightarrow{H_2O_2} \mathrm{ArOH}$$

The reaction may therefore, be of some value in the synthesis of organoboron compounds, or in the synthesis of substances which can normally be prepared from such compounds. However, attempts to prepare biaryls by treating the organic halide with lithium and diborane and treating the resulting reaction mixture with silver nitrate solution and alkali were not successful. In this respect, therefore, the lithium systems differ from similar reactions using Grignard reagents, where the coupling reaction is observed [8], and this suggests that there may be quite significant differences between the reaction systems using different metals. Further investigations are in progress.

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