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REACTIONS OF DIBORANE WITH ORGANIC DERIVATIVES OF LITHIUM, SODIUM, POTASSIUM AND CALCIUM *

F.G. THORPE *, G.M. PICKLES and J.C. PODESTA

Department of Chemistry, University of Lancaster, Lancaster (Great Britain)

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Summary

The reactions of organic halides with diborane in THF in the presence of lithium, sodium, potassium or calcium have been examined. Phenols (or alcohols) are obtained in good yields by hydrogen peroxide oxidation of the products of the above reactions, indicating the formation of organoboron intermediates by a transmetallation process. Arylboronic acids can also be obtained in good yield by the hydrolysis of the products of the reactions involving lithium. These one-step reactions have been shown to be superior to analogous two-step reactions in which pre-formed organolithium reagents are allowed to react with diborane.

Introduction

The reactions of boron halides or esters of boric acid with organometallic compounds are well known as methods of synthesising organoboron compounds, and have been studied in detail for a variety of metals [1]. However, the reactions of organometallic compounds with boron hydrides, particularly diborane, have received comparatively little attention, although the first work in this area was reported by Schlesinger in 1939. Schlesinger examined the reactions of simple alkyl derivatives of aluminum [2], beryllium [3], lithium [4] and gallium [5] and observed the formation of metal borohydrides. Wiberg has studied the reactions of phenyllithium [6] and ethylmagnesium bromide [7] with diborane, and Holliday and Jessop [8] reported the formation of organoboron compounds from a similar reaction using tetramethyl lead.

Most of the above work was limited in scope, and although organoboron compounds are useful intermediates in organic synthesis, the wider synthetic applications were not explored. More recently we have examined certain reaction systems in which intermediates (presumed to be organoboron compounds) formed by reaction of arylmercury [9] or arylthallium [10] compounds with diborane

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* Preliminary Communication: [21].

were found to give phenols on oxidation with alkaline hydrogen peroxide. Similar reactions have been reported for Grignard reagents [11]. The intermediates derived from the mercury and thallium compounds were shown to give arylboronic acids on hydrolysis [12,10].

In this paper we report detailed studies of the nature and possible synthetic uses of the reactions of diborane with the organic derivatives of lithium, sodium, potassium and calcium.

Results and discussion

Organolithium compounds

Two different types of reaction conditions were used in the investigation of the reaction of organolithium compounds with diborane. In the first, a preformed organolithium reagent was reacted with a solution of diborane in tetrahydrofuran (THF) and the resulting reaction mixture was oxidised with alkaline hydrogen peroxide. In the second, a one-stage procedure was employed in which a solution of the organic halide was added directly to a solution of diborane containing pieces of lithium. The reaction mixture was then either oxidised or hydrolysed.

The results of the reaction using preformed organolithium reagents (in THF solution) are shown in Table 1. For three of the five halides, significant final yields of phenols were obtained on oxidation, indicating that organoboron intermediates had been formed by a transmetallation reaction.

$$\mathrm{RLi} + \mathrm{BH_3} \rightarrow \mathrm{R{-}B}\!\Big< \xrightarrow[\mathrm{OH^-}]{\mathrm{H_2O_2}} \mathrm{ROH}$$

The benzyl- and naphthyl-reagents gave coupled and reduced products, respectively; no transmetallation product was detected.

More detailed studies of the phenyllithium systems were then made. The reagent was prepared in ether as solvent by reacting the metal with either bromobenzene or diphenylmercury, and then allowed to react (in a separate stage) with diborane after the concentration of phenyllithium had been determined quantitatively by Gilman's method [13]. The results (Table 2) show that it is difficult to obtain reproducible results, particularly when the reaction is carried

TABLE 1

PRODUCTS OBTAINED AFTER OXIDATION OF INTERMEDIATES FORMED FROM REACTION OF PREFORMED ORGANOLITHIUM REAGENTS (PREPARED FROM Li AND RX) WITH ONE MOLAR EQUIVALENT OF DIBORANE IN THF AS SOLVENT

RX	Yield (%)		
	ROH	RH	RR
Bromobenzene	32		
m-Chlorotoluene	45		
Chlorocyclohexane	20		
1-Chloronaphthalene	0	70	
Benzyl bromide	0		80

TABLE 2

COMPARISON OF YIELDS OF PHENYLLITHIUM AND PHENOL OBTAINED IN THE PREPARATION OF PHENYLLITHIUM IN ETHER AND ITS SUBSEQUENT REACTION WITH DIBORANE (IN THF) AND OXIDATION

Yield (%)		Scale of reactions (mols) [c]
PhLi	PhOH	
94 [a]	86	0.020
75 [a]	72	0.010
71 [a]	70	0.010
37 [a]	35	0.005
95 [b]	90	0.010
42 [b]	40	0.005

[a] PhLi prepared from bromobenzene and lithium. [b] PhLi prepared from diphenylmercury and lithium. [c] Number of moles of bromobenzene or diphenylmercury used to prepare PhLi.

out on a small scale, but it is clear that the overall efficiency of the reaction is dependent on the first step (i.e. the formation of phenyllithium); the transmetallation and subsequent oxidation are almost quantitative. Also, since the final yields of phenol are independent of the method of preparing the phenyllithium, the transmetallation process is not influenced by the presence of lithium halide.

The one-stage version of the above reaction was next examined. Here the organic halide was added directly to a solution of diborane containing pieces of lithium. Preliminary studies showed that phenols can still be obtained by oxidation of the resulting reaction mixture, indicating that the organolithium compound formed in situ undergoes a transmetallation reaction to form the organoboron compound. The reactions of bromobenzene and *m*-chlorotoluene were examined in some detail to determine the most favourable reaction conditions (see Table 3), and this procedure was then applied to a wide range of starting materials. Good yields of phenols were obtained on oxidation of the intermedi-

TABLE 3

EFFECT OF REACTION PARAMETERS ON YIELDS OF PHENOLS OBTAINED BY OXIDISING INTERMEDIATES FROM REACTION OF ORGANIC HALIDES (0.005 mols) WITH DIBORANE IN THF IN THE PRESENCE OF LITHIUM

Bromobenzene		*m*-Chlorotoluene	
Amount of diborane used (mols)	Yield (%) of phenol	Amount of diborane used (mols)	Yield (%) of phenol
0.003 [a]	43	0.003 [a]	45 [f]
0.007 [a]	71	0.007 [a]	65
0.012 [a]	55	0.012 [a]	40
0.032 [a]	36	0.032 [a]	55
0.007 [b]	72	0.007 [b]	68
0.007 [c]	71	0.007 [c]	65
0.007 [d]	68	0.007 [e]	65

[a] 2 h at 20°C, 30 min heated under reflux. [b] 2 h at 20°C. [c] 2 h at −10°C. [d] 2 h at −70°C. [e] 20 min heating under reflux. [f] Toluene in 52% yield was also identified as a product.

ates formed in the reaction (see Table 4) and it was also found that hydrolysis of the intermediates gave significant yields of arylboronic acids. This confirms the presence of organoboron compounds, as well as providing a useful method of preparation of the acids.

Organic derivatives of calcium, sodium and potassium

A number of reactions were examined in which calcium or potassium was used in place of lithium in the one-step process, and the overall yield of phenol determined (see Table 5). In general much poorer yields were obtained, and for the calcium systems, phenols were formed in significant yields only when organic iodides were used as starting materials.

A brief study was made of the use of sodium in these transmetallations. Bromobenzene was reacted with diborane solution in the presence of sodium wire. Although the mixture was vigorously stirred, the surface of the metal soon became dull, and the final yield of phenol was only 6%. A similar reaction was performed, but a large number of glass spheres were added to the reaction vessel in an at-

TABLE 4

YIELDS OF PHENOLS AND ARYLBORONIC ACIDS OBTAINED BY OXIDISING OR HYDROLYSING THE PRODUCTS OBTAINED FROM REACTIONS OF ORGANIC HALIDES (0.005 MOLS) WITH DIBORANE (0.007 MOLS) IN THF IN THE PRESENCE OF LITHIUM

Halide	Yield (%) of phenol	Yield (%) of arylborinic acid
Chlorobenzene	80	45
Bromobenzene	72	58
Iodobenzene	52	
m-Chlorotoluene	68	61
p-Chlorotoluene	56	53
m-Bromotoluene	51	50
o-Bromotoluene	68	
p-Bromotoluene	53	50
p-Chloroanisole	52	46
p-Bromoanisole	42	
m-Bromoanisole	15	
o-Bromoethylbenzene	34	
p-Bromoethylbenzene	68	45
Bromomesitylene	77	
p-Bromophenetole	52	
Benzyl bromide	48	
Chlorocyclohexane	58	
Bromocyclohexane	46	
1-Bromopropane	95	
1-Bromobutane	98	
2-Bromobutane	89, 6[a]	
2-Bromo-2-methylpropane	28, 67[a]	
1-Bromopentane	98	
Bromocyclopentane	69	
1-Bromohexane	99	
1-Bromooctane	84	
1-Bromodecane	85	
1-Bromohexadecane	66	

[a] Yields of alcohol produced by thermal isomerisation of the organoboron compounds.

TABLE 5

YIELDS OF PHENOL OBTAINED BY OXIDISING THE PRODUCTS OBTAINED FROM REACTIONS OF ORGANIC HALIDES (0.005 MOLES) WITH DIBORANE (0.007 MOLES) IN THF IN THE PRESENCE OF A METAL

Halide	Metal	Yield (%) of phenol
Bromobenzene [a]	Ca	1
Bromobenzene [b]	Ca	8
Iodobenzene [a]	Ca	34
Iodobenzene [b]	Ca	48 [d]
m-Iodotoluene [a]	Ca	36
m-Iodotoluene [b]	Ca	33
p-Iodotoluene [a]	Ca	32
p-Iodoanisole [b]	Ca	28
1-Iodohexadecane [a]	Ca	1
Bromobenzene [a]	K	31
Bromobenzene [c]	K	45
o-Bromotoluene [a]	K	25
m-Bromotoluene [a]	K	23
Bromobenzene [a]	Na	28 [e]

[a] 24 h at room temperature. [b] Heated under reflux for 2 h, then left for 24 h. [c] 48 h at room temperature. [d] A 6% yield of $PhB(OH)_2$ was isolated when the intermediate was hydrolysed [e] 48% of unreacted bromobenzene detected at the end of the reaction.

tempt to clean the metal surface; this increased the yield of phenol to 28%, but a large amount of bromobenzene still remained unreacted.

Conclusions

Organic halides react with diborane in THF solution in the presence of lithium to give intermediate organoboron compounds. Subsequent oxidation or hydrolysis of these intermediates gives phenols (or alcohols) or arylboronic acids in good yields. The overall reactions, therefore, provide efficient and simple syntheses of these compounds. This "one-step" process is superior to the analogous reaction using pre-formed organolithium reagents *. The organic derivatives of calcium, potassium and sodium give significant but lower yields of product.

The formation of arylboronic acids suggests that the initially formed organolithium compound undergoes a transmetallation reaction to give mainly RBH_2 or RBH_3^-:

$$RLi + BH_3 \rightarrow RBH_2 + LiH$$
$$RLi + BH_3 \rightarrow RBH_3^- + Li^+$$
$$RBH_3^- + BH_3 \rightarrow RBH_2 + BH_4^-$$

The observation that the yield of arylboronic acid is always less than the corresponding yield of phenol suggests that further reaction to give R_2BH may occur:

$$RBH_2 + RLi \rightarrow R_2BH + LiH$$

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* A recent report [14] 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.

However, arylborinic acids could not be isolated from the hydrolysed products, so this reaction is unlikely to occur to any great extent. The precise reaction sequence probably depends on the relative amounts of starting materials and the particular metal used.

The relative reactivities of the different organometallic species in the transmetallation process are difficult to judge. The overall yield of phenol (or arylboronic acid) is likely to be a reflection of the efficiency of the first part of the reaction, i.e. the formation of the organometallic reagent. The evidence for this is that for those systems using calcium, potassium and sodium which gave a poor overall yield of phenol, considerable quantities of unreacted organic halides were sometimes detected in the final reaction mixture. Also, the 'reactivity' sequence chlorobenzene > bromobenzene > iodobenzene observed for lithium has been observed in other one-step reactions [14] and follows the reactivity of these halides with respect to lithium [15].

Attempts to prepare biaryls by reacting an aryl 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 the corresponding reactions using Grignard reagents, where the coupling reaction has been observed [16], and this suggests there may be significant differences between systems using different metals. Early reports [17] that arylboron compounds undergo reduction rather than a coupling reaction in the presence of silver nitrate are of interest in this context.

A second significant difference between systems using different metals is the affect of excess diborane. For organolithium compounds, a large excess of diborane decreases the amount of transmetallation (as measured by the overall yield of phenol; see Table 3). This is not observed when organomercury compounds are used [9]; for these systems a large excess of diborane is necessary to obtain high yields of phenol.

Experimental

Starting materials

Tetrahydrofuran was purified by heating under reflux with calcium hydride for three hours, and then distilled and stored over a molecular sieve.

Lithium was prepared immediately before use from lithium rod. The rod was washed with petroleum ether and then cut into small pieces which were allowed to drop directly into solvent in the reaction vessel. Potassium and sodium were prepared in a similar manner. Calcium was obtained in the form of granules; these were washed in petroleum ether and cut into smaller pieces prior to use.

The method reported by Brown [18] was used to prepare solutions of diborane in THF. The solution was usually approximately 0.6 *M* in diborane.

Reactions of organolithium compounds with diborane: preparation of phenols

In the two-step reactions, organolithium compounds were first prepared from organic halides and lithium [19] or from lithium and diphenylmercury [20]. The transmetallation reaction was carried out in a three-necked flask fitted with a magnetic stirrer. A slow stream of dry nitrogen was passed through the flask. The diborane solution (usually an equimolar amount, i.e. a two-field excess relative to BH_3) was added to the organolithium reagent (0.005 to 0.02 mol) using a syringe and septum cap. The reaction mixture was stirred for 2 h at room temperature, and then heated under reflux for 30 min. The mixture was cooled and treated slowly with a mixture of 3 *N* sodium hydroxide solution (15 ml) and 30% hydrogen peroxide (23 ml) and then stirred for 30 min. In the aryl systems the mixture was extracted with ether (50 ml in three portions), and this ethereal solution further extracted with three 15 ml portions of sodium hydroxide solution (3 *N*). The aqueous extracts were acidified with sulphuric acid (6 *N*), and extracted with ether. The ether solution was dried, and the concentration of phenol determined quantitatively by GLC and/or UV techniques. (GLC analyses were carried out in an S.E. 30 column in a Pye 104 at temperatures between 100 and 150°C). When alkyllithium reagents were used as starting materials, the solution obtained after oxidation was extracted with ether (50 ml in three portions), the ether solution was dried over magnesium sulphate, and then analysed by GLC.

The one-step reactions were carried out in a three-necked flask fitted with a magnetic stirrer, and a stream of dry nitrogen was passed through the apparatus. Dry THF (10 ml) was placed in the flask, followed by freshly cut pieces of lithium (20% excess). Diborane solution (0.007 mol) was then added, and the organic halide (0.005 mols) was run in from a dropping funnel over a period of 10 min. The reaction mixture was stirred for 2 h, and unreacted lithium was then removed. Work up and determination of yield were carried out as described above.

Reaction of organolithium compounds with diborane: preparation of arylboronic acids

The preparations were carried out on a 0.02 molar scale using the procedure described above for the one-step reaction. However, instead of adding base and peroxide to the intermediate, distilled water (20 ml) was added, the solution was stirred for 30 min, acidified with dilute hydrochloric acid, and extracted with ether (100 ml in four portions). The combined ether extracts were washed with water (10 ml), the solution dried, and the solvent then removed on a rotary evaporator. White solids remained, which were recrystallised from water, weighed and identified by IR, PMR and melting point (all were known compounds).

Reactions of organolithium compounds with diborane: attempted preparation of biaryls

The procedure for the preparation of the intermediate organoboron compounds in solution was carried out as described above for the one-step procedure. The solution was treated with methanol (3 ml) and then with 2 *M* potassium hydroxide solution (12 ml). 5 *M* silver nitrate solution (2.4 ml) was added and the mixture stirred vigorously at room temperature for 1 h. After filtering, the solution was extracted with ether (100 ml in three portions), and the ether solution was analysed by GLC before the solvent was removed. No coupled products (i.e. biaryls) were detected.

Reactions of organic derivatives of calcium, sodium and potassium with diborane

The procedure was exactly analogous to that described for the one-step processes using lithium.

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