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REACTIONS OF DIBORANE WITH LITHIUM DIARYLCUPRATES AND ORGANOCADMIUM COMPOUNDS

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Summary

Lithium diarylcuprates react with diborane to form as intermediates organoboron compounds, which can be converted into phenols, arylboronic acids and arylamines; complexes of triarylboron compounds can also be isolated. Preliminary studies show that organocadmium compounds undergo similar reactions.

Introduction

The organic compounds of boron are important as reagents in organic synthesis. Two well known general methods for their preparation are available; the hydroboration [1] of alkenes to give alkylboranes, and the reactions of boron halides (or esters of boric acids) with organometallic compounds [2]. This second method is applicable to the preparation of both alkyl- and arylboranes. Recently the reactions of organometallic reagents with diborane have been reported; the organometallic compounds studied include those of mercury [3], thallium [4], lithium [5], and tin and lead [6]. These reactions were found to produce intermediates which give phenols (or alcohols) on oxidation with alkaline hydrogen peroxide and boronic acids on hydrolysis. The preparation of phenols from the reaction of Grignard reagents with diborane has also been reported [7]. It was assumed that in all the above processes a transmetallation occurs to give an organoboron intermediate, or intermediates:

$$R{-}M + BH_3 \rightarrow R{-}B\lessdot + [MH]$$

The formation of the products in good yields under mild conditions suggests that the reaction may provide a general route to the formation of organoboron compounds. However, the systems differ in detail. In certain systems [3] the transmetallation is accompanied by reduction (to give RH) and the degree of alkylation or arylation of the boron depends on the particular metal. For example arylborinic acids (R_2BOH) were obtained from the reaction of diborane with organotin [6] and lead compounds, suggesting the formation of diaryl-boron hydrides as intermediates, but only boronic acids (presumed to be derived from monoarylboron hydrides) could be obtained using other organometallic systems. No evidence was obtained to indicate the formation of triarylboron compounds. Since these are important intermediates in organic synthesis incomplete arylation of the boron in the above transmetallations is a disadvantage.

In the present paper we report detailed studies of the nature and synthetic uses of the reactions of diborane with lithium diorganocuprates. Organometallic reagents of this type have been shown to be useful in other areas of organic synthesis, and their properties frequently differ from those of organolithium or magnesium compounds [8]. We also report some preliminary studies of the reaction between diborane and organocadmium compounds.

Results and discussion

Preliminary experiments

Some preliminary experiments were first carried out in order to discover if a transmetallation occurs, and to test a separation procedure based on the assumption that any mono- or di-arylboronhydrides formed can be hydrolysed to the corresponding boronic and borinic acids ($RB(OH)_2$ and R_2BOH) which will be soluble in aqueous alkali, whereas a triarylboron intermediate will be relatively unaffected by water (or dilute alkali) and will be ether soluble. Lithium diphenylcopper was prepared, therefore, from cuprous bromide (1 equivalent) and phenyllithium (2 equivalents) in ether, and reacted with solutions of diborane in THF. The reaction mixtures were then hydrolysed, and the alkaline solutions extracted with ether to give ethereal solutions (A), and aqueous phases (B). The phases were then separately oxidised (using alkaline hydrogen peroxide), and the oxidised solutions analysed for phenol. Experiments were also performed using lithium dibutylcopper, but here the reaction mixtures were oxidised directly.

The results are shown in Table 1. It can be seen that phenol and butanol are

TABLE 1

YIELDS OF PHENOL AND BUTANOL OBTAINED BY OXIDISING PRODUCTS OF REACTION OF DIBORANE WITH R_2CuLi [a]

R	R_2CuLi (mol)	B_2H_6 (mol)	Yield (%) of ROH in A	Yield (%) of ROH in B	Total yield (%) of ROH
C_6H_5	0.015	0.0075	21	7	28
	0.015	0.015	25	12	37
	0.005	0.0075	45	20	65
	0.005	0.010	52	31	83
	0.005	0.0125	33	49	82
C_4H_9	0.010 [b]	0.005			43
	0.010	0.005			40
	0.010 [b]	0.0075			56
	0.010	0.010			71

[a] Reaction conditions: $(C_6H_5)_2CuLi$ reacted for 17 hours and $(C_4H_9)_2CuLi$ reacted for 5 hours with the diborane solution at room temperature. [b] The organolithium cuprate was prepared from RLi and CuI. In all other systems CuBr was used.

formed in the overall reaction in good yields indicating that a transmetallation does occur. The phenol is produced from both the ethereal (A) and aqueous (B) layers, the relative distribution depending markedly on the relative proportions of starting materials. This suggests that triarylboron compounds are formed in the transmetallation. This has not been previously observed.

Preparation of phenols

The procedure described above for lithium diphenylcopper was applied to a number of different lithium diarylcuprates, in order to establish the generality of the reaction, and to examine the product distribution as measured by the yields of phenols in the ethereal and aqueous layers. The conditions chosen were those which gave a maximum overall yield of phenol; these also being the conditions which gave the highest yield of phenol in the ethereal layer. The results are shown in Table 2. For comparison some simple organolithium compounds were also examined using the separation procedure described above (which differs from that used in ref. 5), and these results are also shown in Table 2, together with preliminary studies of similar experiments using diphenylcadmium (prepared from phenyllithium or phenylmagnesium bromide and anhydrous cadmium chloride) in place of the copper or lithium reagents.

Preparation of arylboronic acids, amines, and triarylboron complexes

To check the formation of the different organoboron compounds in the transmetallations, and to investigate further synthetic possibilities, additional reactions of the diaryl cuprates were examined. In one set of experiments the copper reagents were reacted with diborane as described above, and the

TABLE 2

YIELDS OF PHENOLS OBTAINED BY OXIDISING PRODUCTS OF REACTION OF DIBORANE WITH ORGANOMETALLIC REAGENTS [a]

Reagent	Group R	Yield (%) of ROH in A	Yield (%) of ROH in A	Total yield % of ROH
R_2CuLi	C_6H_5	48	28	76
	$pCH_3 \cdot C_6H_4$	75	0	75
	$mCH_3 \cdot C_6H_4$	70	0	70
	$oCH_3 \cdot C_6H_4$	6	88	94
	$pC_2H_5 \cdot C_6H_4$	54	0	54
	$oC_2H_5 \cdot C_6H_4$	3	50	53
	$pCH_3O \cdot C_6H_4$ [b]	49	15	64
	$oCH_3O \cdot C_6H_4$ [b]	0	65	65
R_2Cd	C_6H_5 [c]	50	0	50
	C_6H_5 [d]	38	27	65
RLi	C_6H_5	15	42	57
	$pCH_3 \cdot C_6H_4$	22	47	69
	$mCH_3 \cdot C_6H_4$	19	55	74
	$oCH_3C_6H_4$	19	48	67
	$pCH_3O \cdot C_6H_4$ [b]	8	54	62
	$pC_2H_5 \cdot C_6H_4$	26	52	78

[a] Reaction conditions. The reagent (0.005 mol of R_2CuLi or R_2Cd, or 0.01 mol of RLi) reacted with diborane (0.01 mol) for 17 h at 25°C. [b] Compound RLi prepared from RBr and BuLi. All other organolithium compound prepared from RBr and Li in situ. [c] Prepared from C_6H_5MgBr and $CdCl_2$. [d] Prepared from C_6H_5Li and $CdCl_2$.

TABLE 3

YIELDS OF ARYLBORONIC ACIDS AND AMINES OBTAINED BY HYDROLYSIS OR REACTING WITH HYDROXYLAMINE-*O*-SULPHURIC ACID THE PRODUCTS OF THE REACTION OF R_2CuLi WITH DIBORANE [a]

Group R	Yield (%) of RNH_2 (from A)	Yield (%) of $RB(OH)_2$ (from B)
C_6H_5	—	34
$pCH_3C_6H_4$	25 [b]	4
$mCH_3C_6H_4$	19 [c]	15
$oCH_3C_6H_4$		60
$oCH_3O \cdot C_6H_4$	—	68
$pC_2H_5 \cdot C_5H_4$	16 [c]	—

[a] Reaction conditions. R_2CuLi (0.005 mol) reacted with diborane (0.01 mol) for 17 h at 25°C. [b] Isolated yield of amine. [c] Isolated yield of benzoyl derivative of amine.

reaction mixtures were hydrolysed and ether extracted, but the separate layers (A and b) were not oxidised. Acidification and ether extraction of the aqueous layers led to the isolation of arylboronic acids, and in two systems examined, the addition of a suitable ligand (pyridine or triphenylphosphine) to the ether layer (A) resulted in the formation of white crystalline solids. The IR and PMR spectra of these solids indicated that they were triarylboron complexes of the form $R_3B.L$. The triphenylphosphine complex of tri-*p*-tolyl boron and the pyridine complex of tri-*m*-tolylboron were obtained in 40% and 38% yields respectively.

In a separate set of experiments, three lithium diarylcuprates were reacted with diborane and the ethereal extracts of the hydrolysed reaction mixtures were reacted with hydroxylamine—*O*-sulphonic acid. Arylamines were obtained as products from these reactions; the yields were somewhat low, but this is not unusual in this type of reaction [10].

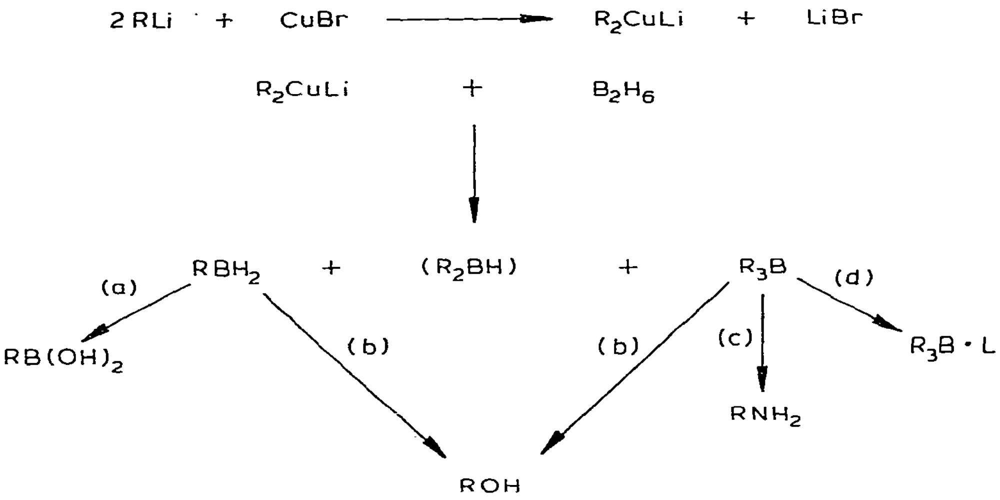
The yields of boronic acids and amines from these separate experiments are shown in Table 3.

Conclusions

Lithium organocuprates and the organic derivatives of lithium and cadmium react readily with diborane to form mixtures of triarylboranes and monoaryl (or alkyl) boron compounds, which can be separated. The reactions are of synthetic value because the monoaryl boron compounds can be hydrolysed to give good yields of arylboronic acids, or oxidised to give phenols. The triarylboranes can be isolated as their complexes (with pyridine or triphenylphosphine), or can be converted into amines or phenols. The overall reaction scheme is shown in Scheme 1 for the lithium organocuprates (although arylborinic acids, R_2BOH, were not isolated in any of the systems).

The composition of the reaction mixture obtained in the transmetallation varies considerably, depending on the particular reaction and conditions. The most important factor is the choice of organometallic compound. The organocuprates and organocadmium compounds give a much higher proportion of triarylborane than similar reactions using organolithium compounds, unless

SCHEME 1



a = hydrolysis   b = oxidation

c = reaction with hydroxylamine-*O*-sulphonic acid

d = reaction with ligand, L (L = $(C_6H_5)_3P$ or C_5H_5N)

orthosubstituted halides are used as starting materials, when the mono-aryl boron compounds predominate. This suggests that steric factors are important. Mono-aryl compounds are also the major products if a high proportion of diborane is used initially, indicating that the aryl transfer to boron take place in a stepwise manner. Another factor may be of importance for the cadmium compounds. Only two systems were examined, but these preliminary experiments indicate that the method of formation of the organocadmium compound (i.e. either from the organolithium compound or the Grignard reagent) may be significant.

In general the organocuprates and cadmium reagents offer distinct advantages over the organic derivatives of mercury [3] and thallium [4], which undergo similar reactions but require a large excess of diborane, and do not give triarylboranes.

Experimental

Starting materials

Tetrahydrofuran was purified by heating under reflux with calcium hydride for three hours, and was stored over a molecular sieve. Ether was dried over sodium. 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. Cadmium chloride was dried by heating to 110°C for several hours (to constant weight) and cooled in a desiccator.

The method reported by H.C. Brown [9] was used to prepare solutions of diborane in THF. The solution was usually approximately 0.6 *M* in diborane.

Reactions of lithium organocuprates with diborane

Organolithium compounds were prepared by the dropwise addition of the aryl halide (0.025 mol) in dry ether (10 ml) to lithium pieces (0.05 mol) in ether (10 ml) under an atmosphere of dry nitrogen, so that a gentle reflux was maintained. A 5 ml aliquot was then analysed by titrating against sulphuric acid (0.1 *N*). The yields of organolithium reagents varied from 82% (for *o*-ethylbromobenzene) to 95% for *p*-bromotoluene. Some of the aryllithium reagent (0.01 mol) was then added via a syringe and septum cap to a slurry of copper(I) bromide (0.005 mol) in ether, at 0°C, under a nitrogen atmosphere. After 10 minutes a solution of diborane (typically 0.010 mol) was added rapidly (using a syringe), and the mixture was stirred for 18 hours at room temperature. The mixture was then hydrolysed by the careful addition of water (15 ml) followed by 3*N* sodium hydroxide solution (5 ml), and this alkaline solution was extracted with two 25 ml portions of ether, giving an ethereal solution (A), and an aqueous phase (B). Different work-up procedures were then used depending on the desired product. Phenols were obtained (from A or B) by oxidation with alkaline hydrogen peroxide solution, using standard procedures [9]. Yields were determined by UV spectroscopy.

Complexes of two triarylboranes were obtained from the dried either phase (A) by the addition of a slight excess of pyridine or triphenyl phosphine. The solutions were stirred at room temperature for twelve hours, and then reduced in volume (on a rotary evaporator) to 20 ml, when white solids formed. The solids were recrystallised from a mixture of ether and petroleum ether, and identified by their IR and PMR spectra. The IR spectra showed no absorption in the region 1300—1400 cm^{-1}, characteristic of boron-oxygen compounds. $(m\text{-}CH_3C_6H_4)_3B.C_5H_5N$, m.p. 127—129°C, PMR (in $CDCl_3$), δ 8.5 (2-H, m, aromatic) 7.0 (15-H, m, aromatic) and 2.3 ppm (9-H, s, methyl). $(p\text{-}CH_3.C_6H_4)_3B.P(C_6H_5)_3$, m.p. 114—116°C, PMR ($CDCl_3$, δ 7.3 (27-H, m, aromatic), 2.4 ppm (9-H, s, methyl).

Arylboronic acids were obtained from the aqueous phase (B). The solutions were acidified with dilute hydrochloric acid and extracted with ether (three 25 ml portions). The combined ether extracts were dried over magnesium sulphate. The ether was then removed, and the solids formed recrystallised from petroleum ether. The acids were identified by their m.p. and IR and PMR spectra.

Arylamines were prepared from the ether solution (A). The ethereal solution was dried over magnesium sulphate and filtered rapidly into a dry 100 ml flask which had been previously flushed with dry nitrogen. A slurry of commercial hydroxylamine-*O*-sulphonic acid (0.01 mol) in dry THF (20 ml) was then added and the mixture was heated under reflux for four hours. The mixture was then cooled and treated with dilute hydrochloric acid (20 ml) and water (30 ml). The aqueous layer was separated from the ether, washed with ether (two 15 ml portions), and then made strongly alkaline with sodium hydroxide solution. This solution was then extracted with ether (three 20 ml portions), and the combined ethereal extracts dried over magnesium sulphate. The amine was then isolated directly by removal of the ether (as for *p*-toluidine) or isolated as the benzoyl derivative. The products were identified by their m.p. and IR and PMR spectra.

Reactions of diphenylcadmium with diborane

Anhydrous cadmium chloride (0.005 mol) was added to a solution of phenyllithium prepared from bromobenzene (0.014 mol) and lithium (0.04 mol) in ether (20 ml) at 5°C. The mixture was then stirred for one hour at room temperature; after this time a Gilman Test [11] for organolithium compounds was negative. Diborane (0.01 mol) in THF was then added to the organocadmium reagent, using a syringe and septum cap, and the mixture was stirred at room temperature for seventeen hours. It was then hydrolysed by the addition of water (20 ml), made alkaline, and extracted with ether (two 25 ml portions).

Phenols were then prepared from the ethereal and aqueous phases, using the procedure described above.

Reactions of organolithium compounds with diborane

Organolithium compounds were prepared in situ in the presence of diborane as described previously [5]. After hydrolysing the reaction mixtures, ethereal and aqueous phases were oxidised separately using the procedure described above.

The solubility of arylboronic acids in ether and dilute aqueous sodium hydroxide solution

In order to test, at least partially, the efficiency of the above separation procedures, an ethereal solution of a boronic acid (*p*-tolyl-boronic and phenylboronic acids) was extracted with dilute sodium hydroxide solution, and the aqueous and ethereal layers separately oxidised. The yields of phenols obtained indicated that under these conditions (which duplicated those used in the main experiments) over 95% of the arylboronic acid had been extracted into the aqueous phase. No phenol was detected in the oxidised ethereal phase.

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