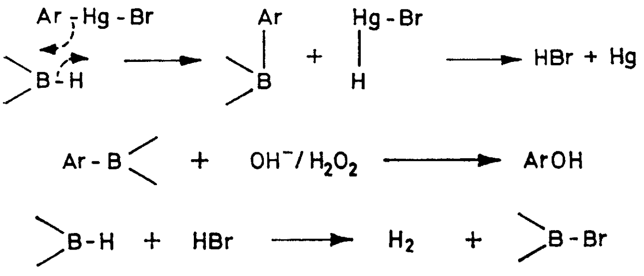
The Reaction of Diborane with Organomercury Compounds; A Synthetic Route to Phenols and Organoboranes

By S. W. BREUER,* M. J. LEATHAM, and F. G. THORPE

(*Department of Chemistry, University of Lancaster, Lancaster*)

Summary Organomercury halides of type ArHgX react with diborane in tetrahydrofuran to give intermediate organoboranes which can be oxidised with alkaline hydrogen peroxide to give high yields of phenols.

ALTHOUGH diborane has proved to be of great value in organic synthesis, very few studies have been made of reactions of diborane with organometallic compounds. Holliday[1] has reported the formation of boron alkyls from diborane and organolead compounds, and dimethylmercury[2] was reported to give trimethylboron in a similar reaction, but for neither of these systems were the synthetic possibilities investigated. We have treated a series of arylmercury compounds with diborane solution in tetrahydrofuran (THF) under normal hydroboration conditions,[3] and without isolating any intermediate compounds, oxidised them with alkaline hydrogen peroxide to the corresponding phenols.



SCHEME

The phenols were produced under conditions which leave organomercury compounds unchanged, and since gas evolution (presumably hydrogen) occurred and metallic mercury was precipitated, the general reaction is probably as shown in the Scheme. The gas evolution provides a convenient indication of the progress of the reaction, which is normally carried out by dissolving the organomercury compound in dry THF and adding to it a standardised solution of B_2H_6 in THF in an atmosphere of dry nitrogen. The solution is stirred at room temperature for periods up to an hour, when water is added to decompose excess diborane and the organoborane is oxidised with alkaline hydrogen peroxide in the usual manner.[3] Typical results are given in the Table.

The results show that increasing the BH_3 concentration results in increased yield of organoborane, but at low BH_3 concentrations another pathway may operate, which results in reduction of the organomercury salt to ArH. This was demonstrated quantitatively in the experiments involving the anisyl and mesityl mercury(II) halides. These were not protonolyses of the intermediate organoboranes, as the ArH compounds were formed in the hydroborating mixture before the addition of water. This suggests the presence of a reducing agent of the borohydride type which may reduce the organomercury compound to ArH, competing with the electrophilic transmetallation.

TABLE

Substrate	Mol BH_3 mol substrate	Reaction time (min)	Yield[a] ArOH (%)	Yield[b] ArH (%)
Ph·HgBr	2	60	15	
Ph·HgBr	8	60	48	
Ph·HgBr	16	60	72	
Ph_2Hg	2	60	53[c]	
Ph_2Hg	16	60	82[c]	
Ph_2Hg	32	60	97·5[c]	
p-Me·C_6H_4·HgCl	2	10	6·5	
p-Me·C_6H_4·HgCl	8	10	45	
p-Me·C_6H_4·HgCl	16	10	99	
m-Me·C_6H_4·HgCl	8	60	70	
p-Me·O·C_6H_4·HgBr	4	60	44	44
p-Me·O·C_6H_4·HgBr	16	60	54	25
p-Me·O·C_6H_4·HgBr	16	10	65	33
p-Cl·C_6H_4·HgCl	8	60	77	
p-HO_2C·C_6H_4·HgCl	8	60	47[d]	2[d]
Mesityl HgCl	16	10	16	78
p-Me_2N·C_6H_4·HgBr	16	60	0	

[a] Determined by u.v.; [b] Determined by g.l.c.; [c] These values represent yields of phenol from *both* phenyl groups; [d] Under the reaction conditions the carboxyl group is reduced to the primary alcohol ($-CO_2H \rightarrow CH_2OH$).

The exact nature of the nucleophilic reducing agent is not known. Although this could be formed from ArHgBr and BH_3, it is more likely to be formed in a reaction involving borane and $HgBr_2$. This is shown by the observation that the reaction of diphenylmercury with borane in the presence of $HgBr_2$ in equimolar (to BH_3) amounts results in an 82% yield of benzene from both phenyl groups in diphenylmercury. Under these conditions no phenol is formed. The $HgBr_2$ is formed in a symmetrisation[4] as evidenced by the fact that diphenylmercury can be isolated from the reaction of PhHgBr and borane.

Since arylmercury compounds are readily available the reactions described in this note provide a useful new method for the synthesis of phenols. Our work also demonstrates that mercury can be efficiently replaced by boron under these conditions, thus opening a new and convenient route to arylboron compounds which are otherwise not easily accessible.

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