Reactions of Organothallium Compounds with Diborane

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ummary A wide range of aryl organothallium compounds react with diborane in tetrahydrofuran solution to give intermediates which on oxidation or hydrolysis give good yields of phenols or arylboronic acids respectively.

RECENT reports have shown that aromatic organomercury compounds react with diborane in tetrahydrofuran (THF) solution to give intermediates which can be oxidized to give phenols as the final products.[1] The organic derivatives of magnesium[2] and lithium[3] also undergo similar reactions. We now report some preliminary studies of the reaction between organothallium compounds and diborane.

TABLE

Yields of phenols and arylboronic acids obtained from reaction of organothallium compounds with diborane.[a]

Ar in $ArTl(OCOCF_3)_2$	Yield (%) of phenol ArOH (a)	(b)	(c)	Yield (%) of $ArB(OH)_2$ (c)
Ph	68	56	58	57
p-MeC_6H_4	75		89	
Mesityl	64	49	38	
p-ClC_6H_4	67	55		
p-BrC_6H_4	67	52	65	39
p-EtC_6H_4	77	59		
3,4-$Me_2C_6H_3$	79	73	81	56
2,4-$Me_2C_6H_3$	83	79	83	62
2,5-$Me_2C_6H_3$	71	75	86	

[a] The organothallium compound and diborane were allowed to react together for (a) 15 h at room temperature, (b) 2 h at room temperature, and (c) 2 h at 65 °C.

The aromatic organothallium trifluoroacetates, $ArTl(OCOCF_3)_2$, prepared by direct substitution of the aromatic compound by thallium(III) trifluoroacetate,[4] were dissolved in dry THF, and treated with a solution of diborane (also in THF). After completion of the reaction, water was added to decompose the excess of diborane and the product was either isolated directly as the arylboronic acid or oxidised further to the corresponding phenol. In a typical reaction, 1 mmol of the organothallium compound was treated with 2·5 mmol of diborane for 15 h at room temperature; the mixture was then either treated with alkaline H_2O_2 solution, using normal hydroboration procedures,[5] when phenols were obtained as products, or excess of distilled water was added, and arylboronic acids could be obtained by extraction with ether. The yields of phenol were determined quantitatively by g.l.c. or u.v. spectroscopy; yields of arylboronic acids were determined by weighing the isolated products.

In additional experiments using a similar procedure, the organothallium compounds and diborane were allowed to react for only 2 h, either at room temperature or at the reflux temperature of THF before oxidation or hydrolysis. The procedure provides a convenient synthesis of phenols and arylboronic acids in reasonable yields under mild conditions, and has wide application because a large range of stable organothallium compounds can be prepared relatively easily.

No attempt has yet been made to isolate the intermediates. However, since the arylboronic acids are produced in quite high yields it seems likely that the species $ArBH_2$ is formed, although the significant differences between the yields of phenols and arylboronic acids demonstrate that other intermediates must also be present and different intermediates may be produced under different conditions.

Attempts to prepare biaryls by treating the intermediate with $AgNO_3$ solution and alkali failed. In this respect the thallium systems differ from similar reactions using Grignard reagents, where the coupling reaction is observed.[6]

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