Tetrahedron Letters No. 42, pp 3719 - 3720, 1974. Pergamon Press. Printed in Great Britain.

THE REACTION OF ORGANOMERCURIALS WITH BORANE: A SYNTHETIC ROUTE TO ARYLBORONIC ACIDS

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(Received in UK 28 August 1974; accepted for publication 12 September 1974)

Recent work (1) has shown that phenols can be obtained in high yields by reacting aromatic organomercury compounds with borane and oxidising the resulting reaction mixture with alkaline hydrogen peroxide. Similar reactions have been reported for organolithium compounds (2) and Grignard reagents (3). The intermediates formed in these reactions were not isolated, and it seemed likely that mixtures of organoboron compounds were produced.

We now wish to report some investigations in which we obtained arylboronic acids by reacting organomercurials with excess borane solution in THF and hydrolysing the resulting reaction mixture. The experimental procedure is extremely simple, and the arylboronic acids are obtained in high yields. In a typical reaction one mmole of organomercury compound was reacted with ten mmoles of borane (BH_3) in THF solution for twenty minutes at room temperature. Distilled water was then added, the mixture filtered (to remove metallic mercury), and the arylboronic acid was obtained by extracting the filtrate with ether. The acid was then recrystallised from water, and characterised by melting point and mass spectrum. The results are shown in the table; yields refer to the pure isolated products.

The results obtained so far do not permit any correlation of structural features in the organomercurial with the yields of arylboronic acid. However, the high yields of acids suggest that the intermediate is $ArBH_2$, which could arise from the transmetallation process:

$$ArHgX + BH_3 \rightarrow ArBH_2 + (HHgX)$$
$$ArBH_2 + H_2O \rightarrow ArB(OH)_2$$

So far the above reaction has been used only in the synthesis of phenols and arylboronic acids. However, it seems likely that slight modifications in the experimental procedure may make possible the synthesis of other types of organoboron compounds. Further investigations are in progress.

We wish to thank the British Council and the O.A.S. for a post-doctorate award (to J.C.P.).

TABLE

Yields of arylboronic acids obtained from reactions of organomercurials with borane

Organomercurial	Arylboronic Acid	% Yield
$(C_6H_5)_2Hg$	$C_6H_5B(OH)_2$	80[a]
C_6H_5-Hg-OAc		68
C_6H_5-Hg-Cl		50
$(p\text{-}CH_3OC_6H_4)_2Hg$	$p.CH_3OC_6H_4\text{-}B(OH)_2$	49[a]
$p\text{-}CH_3OC_6H_4$-Hg-OAc		98
$p\text{-}CH_3OC_6H_4$-Hg-Cl		53
$(p\text{-}CH_3C_6H_4)_2Hg$	$pCH_3C_6H_4B(OH)_2$	76[a]
$p\text{-}CH_3C_6H_4HgCl$		56
$(p\text{-}ClC_6H_4)_2Hg$	$pCl.C_6H_4B(OH)_2$	77[a]
$p\text{-}ClC_6H_4HgCl$		79
$(2\text{-Furyl})_2Hg$	2-Furyl $B(OH)_2$	90[a]
2-Furyl HgCl		97
$(2\text{-Thienyl})_2Hg$	2-Thienyl $B(OH)_2$	80[a]
2-Thienyl HgCl		96

a) These values represent yields of boronic acids from both aryl groups.

References

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