

Reactions of Organothallium Compounds with Diborane ¹

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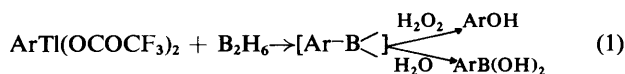
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A number of organothallium(III) compounds of the type $\text{Ar}_n\text{TlX}_{3-n}$ have been treated with diborane in tetrahydrofuran. For $\text{X} = \text{OCOCF}_3$ and $n = 1$ a transmetallation occurs to give organoboron intermediates which, on hydrolysis or oxidation, give arylboronic acids or phenols, respectively, in yields of ca. 70%. Reasonable yields are also obtained when $\text{X} = \text{Cl}$ or OCOCH_3 and $n = 2$, but little or no transmetallation occurs when $\text{X} = \text{Cl}$ or CN and $n = 1$.

Alkylboranes have been used extensively as reagents in organic synthesis.² The normal method of preparation by the hydroboration of alkenes² is naturally not applicable to arylboron compounds, and so we have examined the reactions of diborane with arylorganometallic compounds as a method of forming such compounds as intermediates in synthesis. The first work in this area was reported by Schlesinger³ in 1939, but was concerned with the preparation of metal borohydrides. Other synthetic possibilities were not examined until comparatively recently, when the organic derivatives of mercury,⁴ lithium,⁵ and tin⁶ were found to react with diborane to give intermediates which gave phenols on oxidation and arylboronic acids on hydrolysis. We report here studies of the reactions of diborane with organothallium compounds. Thallium compounds were chosen since a wide range of organic derivatives can be prepared by the direct thallation⁷ of aromatic compounds.

Results and Discussion

Preliminary experiments were first carried out, using four different arylthallium(III) bis(trifluoroacetates), under a variety of reaction conditions to determine whether or not transmetallation occurred and, if it did, the optimum conditions. The thallium compound was dissolved in dry tetrahydrofuran (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 $[\text{ArB}(\text{OH})_2]$, or oxidised to the corresponding phenol using alkaline hydrogen peroxide [equation (1)].



The yields of phenols were determined quantitatively by u.v. spectroscopy and yields of arylboronic acids were determined by weighing the isolated products. The results (Table 1) showed that product yields were relatively high when an excess of diborane was used. Significantly lower yields were obtained when the amount of diborane used was decreased, and a very large excess of diborane also resulted in some decrease in yield. Satisfactory conversions were obtained using a molar ratio of diborane to thallium of 2.5:1. Using this ratio of reactants, a range of different arylthallium(III) bis(trifluoroacetates) was used to examine the effect of structural changes in the aryl group on the yields of phenols and boronic acids. Substituents in the aromatic ring appeared to have only small effects, and yields of about 70% were usually obtained (Table 2). As an exception, however, no phenol or boronic acid could

Table 1. Effect of reaction conditions on yields of phenols or arylboronic acids obtained from the reaction of arylthallium(III) compounds with diborane

Ar in $\text{ArTl}(\text{OCOCF}_3)_2$	Molar ratio $\text{B}_2\text{H}_6 : \text{ArTlX}_2$	Reaction time (h)	Product yield (%)
<i>p</i> -ClC ₆ H ₄	2.5	0.25	15 ^a
<i>p</i> -ClC ₆ H ₄	2.5	1.0	31 ^a
<i>p</i> -ClC ₆ H ₄	2.5	2.0	55 ^a
<i>p</i> -ClC ₆ H ₄	2.5	15.0	67 ^a
<i>p</i> -Et·C ₆ H ₄	0.5	2	31 ^a
<i>p</i> -Et·C ₆ H ₄	1.0	2	35 ^a
<i>p</i> -Et·C ₆ H ₄	2.5	2	59 ^a
<i>p</i> -Et·C ₆ H ₄	5.0	2	77 ^a
<i>p</i> -Et·C ₆ H ₄	10.0	2	69 ^a
2,5-Me ₂ C ₆ H ₃	0.5	2	32 ^a
2,5-Me ₂ C ₆ H ₃	2.5	2	75 ^a
2,5-Me ₂ C ₆ H ₃	5.0	2	73 ^a
2,5-Me ₂ C ₆ H ₃	10.0	2	43 ^a
<i>p</i> -MeC ₆ H ₄	0.5	2	0 ^b
<i>p</i> -MeC ₆ H ₄	2.5	2	50 ^b
<i>p</i> -MeC ₆ H ₄	5.0	2	94 ^b

^a Yield of phenol obtained on oxidation of reaction intermediate, determined quantitatively from u.v. spectra. ^b Yield of arylboronic acid isolated after hydrolysis of reaction intermediate.

be detected in the reaction using *p*-methoxyphenylthallium trifluoroacetate.

In a third set of experiments, the effect on yield of replacing the trifluoroacetate group by halide, cyanide, or acetate was examined, and some diarylthallium compounds were also used (Table 3). The arylthallium dichlorides and cyanides showed little tendency to undergo a transmetallation with diborane, although diphenylthallium chloride and di-*p*-tolylthallium acetate gave reasonable yields of organoboron intermediates (as judged by the yield of phenol produced on oxidation). An increase in the relative proportion of diborane produced an increase in yield, *i.e.* the same trend as that observed for the arylthallium bis(trifluoroacetates).

In all the reactions of the arylthallium bis(trifluoroacetates) studied, a white solid was precipitated when the diborane solution was added to the solution of the thallium compound in THF. Qualitative tests showed this precipitate to be a thallium(I) salt. It was also noted that a gas (assumed to be hydrogen) was evolved during the addition.

All the above results demonstrate that when an excess of diborane reacts with an arylthallium(III) compound a transmetallation occurs in which the aryl group is transferred to boron, the best results being obtained using trifluoroacetates. The intermediates give phenols on oxidation, but attempts to prepare diaryls by treating the intermediates with silver nitrate solution failed (although this coupling reaction has

Table 2. Yields of arylboronic acids and phenols obtained from the reaction of diborane with arylthallium(III) bis(trifluoroacetates) in the molar ratio 2.5 : 1^a

Ar in ArTl(OCOCF ₃) ₂	Yield (%) of phenol ArOH			Yield of ArB(OH) ₂ (c)
	(a)	(b)	(c)	
Ph	58	56	68	57
<i>p</i> -MeC ₆ H ₄	89		75	50
Mesityl	38	49	64	85
<i>p</i> -ClC ₆ H ₄		55	67	52
<i>p</i> -BrC ₆ H ₄	65	52	67	52
<i>p</i> -EtC ₆ H ₄		59	77	72
2,5-Me ₂ C ₆ H ₃	86	75	71	61
3,4-Me ₂ C ₆ H ₃	81	78	79	56
2,4-Me ₂ C ₆ H ₃	83	79	83	52
<i>p</i> -MeOC ₆ H ₄	1		2	0
<i>p</i> -CF ₃ C ₆ H ₄	33	30	36	

^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.

Table 3. Yields of phenols obtained from the reaction of diborane with compounds Ar_nTlX_{3-n} in THF^a

Ar _n TlX _{3-n}	Molar ratio B ₂ H ₆ : Ar _n TlX _{3-n}	Yield (%) of phenol ArOH ^b
Ph ₂ TlCl	2.5	48
Ph ₂ TlCl	0.5	23
PhTlCl ₂	2.5	8
PhTlCl ₂	0.5	0
PhTl(CN) ₂	2.5	4
PhTl(CN) ₂	0.5	0
Ph ₂ TlCN	2.5	4
Ph ₂ TlCN	0.5	0
(<i>p</i> -MeC ₆ H ₄) ₂ TlOAc	2.5	25

^a Reactants heated for 2 h at 65 °C, then oxidised. ^b Yields of phenols based on total number of aryl groups present.

been reported⁸ for similar reactions using Grignard reagents). On hydrolysis arylboronic acids are formed as the main product, suggesting that the principal intermediate is a mono-arylborane, ArBH₂ (or ArBH₃⁻). An unstable thallium(III) hydride may also be produced, decomposition of which could explain the formation of thallium(I) salts and gas evolution [thallium(III) hydride has been reported,⁹ but it decomposes at 0 °C to give thallium(I) hydride and hydrogen, and unstable hydrides of mercury have also been reported¹⁰]. However, this would suggest that the ratio of hydrogen produced to thallium compound used should equal one, whereas the observed ratio was close to three (at room temperature), so other reactions must accompany transmetallation. For the reactions of 2,5-dimethylphenyl- and *p*-methoxyphenylthallium(III) bis(trifluoroacetates) with diborane, it was shown that reduction (to 2,5-dimethylbenzene and anisole) occurred, and it is probable that some reduction takes place in all the reactions.

The results (Table 2) show that the yields of arylboronic acids are frequently lower than those of the corresponding phenols. This suggests that in some systems further reaction to give diaryl- or triaryl-boron compounds occurs. However, no diarylboronic acids (or triarylboranes) could be isolated from the reaction after hydrolysis.

The mechanism of the transmetallation is not known. With the exception of the *p*-methoxyphenyl compound, the general order of reactivity of the aryl groups roughly parallels that in

electrophilic substitution, but the nature of X in ArTlX₂ is the most important factor. Trifluoroacetates or acetates give higher yields than chlorides, so initial complexation between the carbonyl group and boron may be important.

Experimental

Tetrahydrofuran (THF) was dried using standard procedures. The method reported by Brown¹¹ was used to prepare solutions of diborane; the solution was usually *ca.* 0.6M in diborane. Arylthallium(III) bis(trifluoroacetates) were prepared by direct thallation using thallium(III) trifluoroacetate.⁷ Other thallium compounds were prepared using standard procedures.^{12a,b,c} Ether refers to diethyl ether throughout.

Reactions of Organothallium Compounds with Diborane.—The organothallium compound (0.002 mol) was placed in a 100-ml 3-necked flask, dry THF (10 ml) was added, and the solution was stirred magnetically under a slow stream of dry nitrogen. Diborane solution (typically 0.005 mol, *ca.* 10 ml of solution) was added rapidly *via* a septum cap using a syringe (some white precipitate was usually formed at this stage). The stirred mixture was then heated under reflux for 2 h (see Tables for details of other reaction times and temperatures), and then cooled to 0 °C. Distilled water (5–10 ml) was added dropwise to decompose the excess of diborane and hydrolyse the reaction products. Different work-up procedures were then used depending on the desired product, as follows.

Formation of Boronic Acids.—More distilled water (30 ml) was added to the above solution, the mixture stirred at room temperature for 30 min., and then extracted with ether (3 × 15 ml). The combined ether extracts were dried (MgSO₄) and the solvent removed under reduced pressure. The white solid remaining was recrystallised from water and identified as the boronic acid by m.p., i.r. and ¹H n.m.r. spectra. In several experiments the white solid obtained above was extracted with *n*-pentane; ethanolamine was added to the pentane extracts in an attempt to isolate diarylboronic acids as their ethanolamine complexes, but no such complexes could be isolated.

Formation of Phenols.—After the addition of water to decompose the excess of diborane (see above), a mixture of aqueous 3M-sodium hydroxide solution (3 ml) and 30% hydrogen peroxide (5 ml) was slowly added and the resulting mixture stirred for 30 min. Ether (30 ml) was added, and the mixture extracted with 3M-sodium hydroxide solution (3 × 10 ml). The combined aqueous extracts were acidified with dilute hydrochloric acid and extracted with ether (3 × 20 ml). The ether extracts were combined, made up to a known volume with ether, and the yield of phenol determined quantitatively by u.v. spectroscopy, using standard calibration curves prepared for each phenol.

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