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Transmetallations between aryltrialkyltins and borane: synthesis of arylboronic acids and organotin hydrides

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Abstract

Aryltrialkyltin compounds react with borane in THF to give mixtures of trialkyltin hydrides and arylboranes, which on hydrolysis give arylboronic acid in high yields. The arylboronic acids are easily separated and obtained free of organotins.

Keywords: Transmetallations; Aryltrialkyltins; Borane; Organotin hydrides; Arylboronic acids

1. Introduction

Arylboronic acids are valuable reagents for organic synthesis. Thus, they have lately been employed in the synthesis of achiral and chiral alcohols [1], of diaryl ethers [2], and are also currently used for palladium-catalyzed cross-coupling reactions with organic halides or triflates leading to the formation of carbon-carbon bonds (Suzuki reaction) [3]. The boronic acids are generally prepared via the reaction of boron halides (or esters of boric acid) with organometallic compounds [4]. The yields, however, are usually fairly modest (ca. 50%). A more recent procedure for the synthesis of arylboronic esters in high yields (ca. 80%) is the Pd(0)-catalyzed cross coupling reaction of the pinacol ester of diboron with haloarenes [5]. The exchange reactions between borane in THF and arylmetallic derivatives of Li, Na, K, Ca [6a], Hg [6b], Tl [6c], Pb [6d], Sn [6d,e], and Mg [7] also lead to arylboronic acids. With most of the organometallic compounds studied the yields were low (9% to a maximum of ca. 60%) due, in some cases, to the formation of other organoboron derivatives such as borinic acids and triarylboron. It should be noted that the best results were obtained using high borane/organometallic compound ratios (four- to tenfold excess of borane).

Taking into account that the tin-sp^3 carbon bond does not react with borane in THF [8], we considered of interest to study the reactions between aryltrialkyltin compounds and borane in THF as a potentially useful route to arylboronic acids and organotin hydrides.

2. Results and discussion

Preliminary experiments were first carried out, using phenyltri-*n*-butyltin, under a variety of reaction conditions to determine whether or not transmetallation occurred and, if it did, the optimum conditions.

The organotin compound was dissolved in dry THF and treated with a solution of borane in the same solvent. After completion of the reaction, water was added to transform the arylborane into the corresponding arylboronic acid and to eliminate any excess of borane. We found that the hydrolysis of the reaction mixtures led to phenylboronic acid and tri-*n*-butyltin hydride in good to excellent yields according to the reaction conditions, as shown in Scheme 1 (R = *n*-Butyl, Ar = Phenyl).

These studies included variations of the borane/phenyltri-*n*-butyltin ratios in the range of 1–8 and of the times of heating under reflux in the range of 1–4 h. The optimum conditions found were a ratio borane/

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$$R_3SnAr + BH_3 \xrightarrow{THF} R_3SnH + ArBH_2 \xrightarrow{H_2O} Ar\text{-}B(OH)_2$$

Scheme 1. Exchange reactions between aryltrialkyltin compounds and borane in THF.

organotin of 1.05 and 1 h heating. Under these reaction conditions tri-*n*-butyltin hydride was obtained in 85% yield and phenylboronic acid in 96% yield. It should be noted that, although longer periods of heating do not affect the yield of tin hydride they do diminish the yields of phenylboronic acid, probably due to the thermal decomposition of the intermediate phenylborane. We then studied the reaction of a series of aryltri-*n*-butyltins and phenyltrialkyltins with borane in THF, under the same reaction conditions, and found that these reactions also lead to mixtures of trialkyltin hydrides and arylboronic acids, in most cases with excellent yields. The results obtained are summarized in Table 1.

As shown in Table 1, only in the case of 1-naphthyl derivatives (entries 6 and 7) was the formation of product of reduction (naphthalene) observed. In Table 1 it can also be seen that the size of the alkyl ligands (entries 8 and 9) affect the yields of products to some extent. Thus, in the case of the octyl ligand (entry 8) whereas the yield of the triorganotin hydride is the same as that obtained when the alkyl ligand was butyl (entry 1), the yield of phenylboronic acid is lower. In the case of the dodecyl ligand (entry 9), the yields of both tin hydride and phenylboronic acid are noticeable lower compared with the yields obtained with the butyl ligand (entry 1).

The mixtures of arylboronic acids and organotin hydrides thus obtained can then be easy and completely separated by column chromatography on silica gel 60, the organotin hydrides being eluted with hexane and the arylboronic acid with hexane–diethyl ether (1:1). The arylboronic acids were then recrystallized from water; their melting points were coincident with those reported in the literature and the mixed melting points with authentic samples showed no depression. ^{1}H- and ^{13}C-NMR spectra also showed that the boronic acids were completely free of organotin residues. It should be noted that the organotin hydrides could be either employed for performing their typical reactions or reconverted into the starting trialkyltin chloride through their reaction with carbon tetrachloride.

Table 1
Reactions of aryltrialkyltin compounds with borane in THF [a]

Entry	Ar	R	Ar–B(OH)$_2$ (%) [b]	R_3SnH (%) [b]
1	Phenyl	*n*-Butyl	96	85
2	*o*-Tolyl	*n*-Butyl	83	86
3	*p*-Tolyl	*n*-Butyl	85	84
4	*o*-Anisyl	*n*-Butyl	85	90
5	*p*-Anisyl	*n*-Butyl	88	91
6	1-Naphthyl	*n*-Butyl	48 [c]	72 [c]
7	1-Nahphtyl	*n*-Butyl	68 [d]	95 [d]
8	Phenyl	*n*-Octyl	80	86
9	Phenyl	*n*-Dodecyl	71	78

[a] One hour heating except when otherwise stated.
[b] Yields of pure, isolated products (average of five experiments).
[c] Also starting organotin and 26% of reduction product (naphthalene).
[d] Three hours heating; 32% of reduction.

In summary, we have developed a method for a quick and low cost synthesis on a preparative scale of arylboronic acids and trialkyltin hydrides in high yields. The trialkyltin moiety, used as a 'carrier' of the aryl groups, is recovered in high yield after the reactions and could be reused. The method also has the advantage that the arylboronic acids are obtained pure and uncontaminated by organotin residues and by other organic and inorganic boron derivatives as well as free of halides. The only limitation of this method is that it is restricted to those aryl derivatives with substituents that do not react with Grignard reagents.

3. Experimental

The starting tri-*n*-butylphenyl- and tri-*n*-butyl-1-naphthyltin compounds were obtained from the reaction between tri-*n*-butyltin chloride and the corresponding arylmagnesium derivatives [9]. Following the same procedure, *o*-anisyltri-*n*-butyltin, *p*-anisyltri-*n*-butyltin, *o*-tolyltri-*n*-butyltin, *p*-tolyltri-*n*-butyltin, phenyltri-*n*-octyltin, and phenyltri-*n*-dodecyltin were also obtained, their ^{1}H- and ^{13}C-NMR characteristics are shown below.

All the exchange reactions were carried out following the same technique. One reaction is described in detail in order to illustrate the method used.

To a stirred solution of phenyltri-*n*-butyltin (1 g, 2.7 mmol) in dry THF (10 ml), was added a solution of borane in THF (0.0028 mmol, 1.8 ml of a 1.58 M solution). The preparation was carried out under an atmosphere of nitrogen. The mixture was left at room temperature for 1 h and then refluxed during 1 h. After cooling, diethyl ether (10 ml) and water (0.1 ml) were added, the solution was dried with magnesium sulphate, and the solvent was removed under vacuum. The crude product was purified by column chromatography (silica gel 60), tri-*n*-butyltin hydride (0.67 g, 0.0023 mmol, 85%), ν_{Sn-H} 1811 cm^{-1} (Ref. [10], p. 68, 1811 cm^{-1}), being eluted with hexane and phenylboronic acid (0.317 g, 0.0026 mmol, 96%) with hexane–diethyl ether (1:1). After one recrystallization from water, the phenylboronic acid gave m.p. 214–216°C (Ref. [10] 216°C). The mixed m.p. with an authentic sample [6d] showed no depression.

Following the same procedure we obtained the known [4,10,11] tri-*n*-octyl- (ν_{Sn-H} 1815 cm^{-1}) and tri-*n*-dodecyltin hydrides (ν_{Sn-H} 1806 cm^{-1}), as well as *p*-tolylboronic acid (m.p. 242–243°C), *o*-tolylboronic acid (m.p. 168°C), *p*-anisylboronic acid (m.p. 202–204°C), *o*-anisylboronic acid (m.p. 165°C), and 1-naphthylboronic acid (m.p. 182–183°C).

3.1. ^1H- and ^{13}C-NMR of the new aryltrialkylcompounds[2]

3.1.1. o-Anisyltri-n-butyltin

δ_H: 0.80 (t, 9H, $J = 7.5$); 0.95 (t, 6H, $J = 7.4$) 1.24 (m, 6H); 1.44 (m, 6H); 3.69 (s, 3H); 6.73 (d, 1H, $J = 8.7$), 6.87 (m, 1H); 7.22 (m, 1H); 7.28 (d, 1H, $J = 6.7$). δ_C: 10.12 (332.4); 14.11; 27.75 (30.1); 29.55 (21.4); 55.41; 109.28 (21.4); 121.25 (38.9); 130.03; 130.71 (367.3); 137.34 (31.2); 164.15.

3.1.2. p-Anisyltri-n-butyltin

δ_H: 0.88 (t, 9H, $J = 7.4$); 1.02 (t, 6H, $J = 8.2$); 1.32 (m, 6H); 1.52 (m, 6H); 3.78 (s, 3H); 6.90 (d, 2H, $J = 8.1$); 7.37 (d, 2H, $J = 8.5$). δ_C: 9.09 (325.06); 13.58; 26.89 (30.8); 28.62 (19.8); 54.77; 113.72 (21.7); 131.84 (364.5); 137.13 (35.5); 159.59.

3.1.3. o-Tolyltri-n-butyltin

δ_H: 0.97 (t, 6H, $J = 7.3$); 1.16 (t, 9H, $J = 8.3$); 1.42 (m, 6H); 1.62 (m, 6H); 2.48 (s, 3H); 7.17–7.33 (m, 3H); 7.48 (m, 1H). δ_C: 10.43 (336.4); 14.12; 25.45 (23.2); 27.87 (60.3); 29.62 (20.4); 125.30 (42.6); 128.71; 129.28 (34.8); 136.94 (31.0); 142.40 (359.6); 145.04.

3.1.4. p-Tolyltri-n-butyltin

δ_H: 0.88 (t, 6H, $J = 7.2$); 1.03 (t, 9H, $J = 7.3$); 1.33 (m, 6H); 1.52 (m, 6H); 4.10 (s, 3H); 7.14 (d, 2H, $J = 7.4$); 7.35 (d, 2H, $J = 7.5$). δ_C: 9.40 (324.3); 13.55; 21.27; 27.27 (57.5); 28.98 (20.4); 128.75 (40.4); 136.34 (32.6); 137.48 (379.7); 137.73.

3.1.5. Phenyltri-n-octyltin

δ_H: 0.93 (t, 6H, $J = 6.9$); 1.09 (t, 9H, $J = 7.7$); 1.20–151 (m, 36H); 7.36 (m, 2H); 7.51 (m, 3H). δ_C: 9.80 (338.6); 14.00; 22.59; 26.76 (20.8); 29.08; 29.20; 33.56; 34.32 (53.2); 127.81 (39.0); 127.82 (39.0); 128.63; 141.99 (360.5).

3.1.6. Phenyltri-n-dodecyltin

δ_H: 0.80 (t, 6H, $J = 6.6$); 0.96 (t, 9H, $J = 7.7$); 1.05–1.71 (m, 60H); 7.20 (m, 2H); 7.36 (m, 3H). δ_C: 9.85 (338.9); 13.9; 22.60; 26.75 (20.5); 29.12; 29.28; 29.54; 29.56; 29.58; 29.61; 31.86; 34.30 (53.6); 127.79; 127.82 (41.1); 136.39 (31.2); 142.03 (394.9).

[2] In $CDCl_3$; chemical shits, δ, in ppm with respect to TMS, in ^1H spectra, and to $CDCl_3$ in ^{13}C spectra; ^3J (H,H) and ^nJ (Sn,C) coupling constants in Hz (in brackets).

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