APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2007; **21**: 682–687

(www.interscience.wiley.com) DOI:10.1002/aoc.1225

Three-step synthesis of arylpolyboronic acids from phenols via organotin compounds

Pablo M. Fidelibus[1,2], Gustavo F. Silbestri[1,2], María T. Lockhart[1], Sandra D. Mandolesi[1], Alicia B. Chopa[1,2]* and Julio C. Podestá[1,2]*

[1]INIQO, Departamento de Química, Universidad Nacional del Sur, Av. Alem 1253, 8000, Bahía Blanca, Argentina
[2]CONICET, Buenos Aires, Argentina. 3, Comisión de Investigaciones Científicas, Provincia de Buenos Aires, La Plata, Argentina

Received 20 December 2006; Revised 16 January 2007; Accepted 2 February 2007

In this paper we describe a three-step synthesis of aryldi- and triboronic acids starting from phenols. Several substituted phenols (I) were converted into the corresponding aryldiethylphosphates (II) in good to excellent yields. The latter, on reaction with sodium trimethylstannide in liquid ammonia, under irradiation, afforded the aryl- and heteroarylpoly(trimethylstannyl) derivatives in 65–90% yield. The third step is the reaction of the organotin compounds with borane in THF, which leads to the corresponding arylpolyboronic acids in around 80% yield. In order to confirm their structure, some of the diboronic acids were converted into the corresponding pinacol esters. The results obtained in a study on the synthesis of various terphenyls through double and triple Suzuki couplings catalyzed by palladium acetate between the obtained arylpolyboronic acids and various aryl halides are also reported. These reactions proceeded with an average 65% yield, and also enabled us to confirm the structures of some of the diboronic acids. The structure of the new compounds was determined by ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy, mass spectrometry and IR spectroscopy. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: SRN1 reactions; arylpoly(trimethyltin) compounds; borane; transmetallations; arylpolyboronic acids; Suzuki reactions; aromatic polycyclic hydrocarbons

INTRODUCTION

Arylboronic and aryldiboronic acids are very useful intermediates in organic synthesis,[1] in polymer chemistry[2,3] and they are also used as flame retardants.[4] The first synthesis of 1,4- and 1,3-benzenediboronic acids via the reaction between the lithium and Grignard reagents of the corresponding benzene dibromides and methyl borate was reported in 1957.[5] Other authors improved this procedure by obtaining 1,4- and 1,3-benzenediboronic acids in 50–60% yield.[6] We have recently reported the synthesis of benzene- and pyridinediboronic acids in 79–83% yield via exchange reactions between bis(trimethylstannyl) aromatic compounds and borane in THF.[7]

On the other hand, trialkylstannyl- and poly(trialkylstannyl)substituted aryl- and heteroaryl compounds are now easily available via $S_{RN}1$ reactions of trimethylstannyl anions with aryldichlorides,[8,9] chloroaryltrimethyl ammonium iodides,[10] and aryl- and heteroaryl diethylphosphates[11–13] in liquid ammonia [equation (1)].

Taking into account these previous results, we considered of interest a study on the scope of these reactions as well as of the use of aromatic polyboronic acids as starting material for the synthesis of polycyclic aromatic systems via Suzuki cross coupling reactions.

EXPERIMENTAL

^{1}H, ^{13}C and ^{119}Sn NMR spectra were obtained in a Bruker ARX 300 instrument at 300 K, in 5 mm diameter tubes,

---

*Correspondence to: Julio C. Podestá and Alicia B. Chopa, Universidad Nacional del Sur, Departamento de Quimica, Avenida Alem 1253 8000 Bahia Blanca, Argentina.
E-mail: jpodesta@uns.edu.ar; achopa@uns.edu.ar

Contract/grant sponsor: Consejo Nacional de Investigaciones Científicas y Técnicas, CONICET, Argentina.
Contract/grant sponsor: Universidad Nacional del Sur (Bahía Blanca, Argentina).
Contract/grant sponsor: Comisión de Investigaciones Científicas, Provincia de Buenos Aires, La Plata, (CIC, Argentina).
Contract/grant sponsor: Alexander von Humboldt Foundation (Germany) are gratefully acknowledged..

using 10% (w/v) solutions of the compounds. Mass spectra were obtained using a Hewlett Packard CGL-Ms 6890/5972 equipment. Melting points were determined in a Kofler hot stage and are uncorrected. Sample irradiations were carried out in an irradiator constructed in this laboratory consisting of four water-cooled mercury lamps of 250 W emitting maximally at 350 nm. All the solvents and reagents used were analytical reagent-grade. Infrared spectra were recorded with a Nicolet Nexus FT spectrometer. Phenols (I) were converted into the corresponding aryl diethyl phosphate esters (II) by the reaction with diethyl phosphite and triethylamine in CCl_4 solution.[14]

Synthesis of aryl- and heteroaryl organotin compounds: photostimulated reactions of aryl diethyl phosphates with Me_3SnNa in liquid ammonia

The synthesis and physical characteristics of organotin compounds **5**,[15] **7**,[16] **9**,[13] **10**,[14] and **11**[13] have already been reported. All the reactions were carried out following the same procedure. One experiment is described in detail in order to illustrate the method used.

*Synthesis of 2,7-bis(trimethylstannyl)naphthalene (**6**)*

Into a 100 ml two-necked round-bottomed flask, equipped with a coldfinger condenser charged with acetone–liquid nitrogen, a nitrogen inlet and a magnetic stirrer, were condensed 70 ml of sodium-dried ammonia. Me_3SnCl (0.438 g, 2.20 mmol) was dissolved and sodium metal (0.116 g, 5.06 mg atom) was added until the blue color persisted for at least 5 min. When the blue color disappeared, 2,7-bis[(diethoxyphosphoryl)oxy]naphthalene (**2**) (0.432 g, 1.00 mmol) was added and the resulting solution was then irradiated (see above) with stirring for 4 h. The reaction was quenched by adding NH_4Cl in excess, and the ammonia was allowed to evaporate. The residue was treated with water and then extracted with diethyl ether. Ether extracts were washed with brine and dried over anhydrous magnesium sulfate. Removal of the solvent gave 0.420 g of crude product as a powder which was recrystallized from ethanol, leading to **6** (0.344 g, 0.75 mmol, 75%) as a brown solid: m.p. 84–86 °C. ^1H NMR ($CDCl_3$) δ 0.39 [s, 18H, $^2J(^{119}Sn,H)$ 52.8]; 7.58 [d, 2H, $^3J(H,H)$ 7.8, $^3J(^{119}Sn,H)$ 37.9]; 7.77 [d, 2H, $^3J(H,H)$ 7.8, $^4J(^{119}Sn,H)$ 9.8]; 7.98 [s, 2H, $^3J(^{119}Sn,H)$ 50.7]. $^{13}C\ \{^1H\}$ NMR ($CDCl_3$) δ −9.1 [$^1J(^{119}Sn,{}^{13}C)$ 350.4]; 127.3 [$^3J(^{119}Sn,{}^{13}C)$ 44.6]; 132.7 [$^2J(^{119}Sn,{}^{13}C)$ 38.2]; 133.4 [$^3J(^{119}Sn,{}^{13}C)$ not observed]; 133.7 [$^4J(^{119}Sn,{}^{13}C)$ 8.8]; 136.1 [$^2J(^{119}Sn,{}^{13}C)$ 34.0]; 140.2 [$^1J(^{119}Sn,{}^{13}C)$ 460.0]. ^{119}Sn NMR ($CDCl_3$) δ −27.6. MS m/z (relative intensity): 456 (7) $[M]^+$; 441 (100) $[M\text{-}15]^+$; 411 (24) $[C_{13}H_{15}Sn_2]^+$; 396 (3) $[C_{12}H_{12}Sn_2]^+$; 381 (24) $[C_{11}H_9Sn_2]^+$; 366 (14) $[C_{10}H_6Sn_2]^+$; 165 (20) $[C_3H_9Sn]^+$; 135 (34) $[CH_3Sn]^+$; 120 (60) [Sn]. Analysis, found : C, 42.45; H, 5.42; calcd for $C_{16}H_{24}Sn_2$ (453.78) : C, 42.35; H, 5.33%.

*2,2-bis[4-(Trimethylstannyl)phenyl]propane (**8**)*

The procedure described for compound **6** was followed using 2,2-bis{4-[(diethoxyphosphoryl)oxy]phenyl}propane (**4**) (1.00 mmol). The crude product recrystallized from ethanol gave 0.445 g (0.85 mmol, 85%) of **8** as a white solid: m.p. 105–107 °C. ^1H NMR ($CDCl_3$) δ 0.09 [s, 18 H, $^2J(^{119}Sn,H)$ 55.0]; 1.50 (s, 6H); 7.32–6.95 (m, 8H). $^{13}C\ \{^1H\}$ NMR ($CDCl_3$) δ −9.2 [$^1J(^{119}Sn,{}^{13}C)$ 350.0]; 30.9; 43.2; 126.9 [$^2J(^{119}Sn,{}^{13}C)$ 45.8]; 135.9 [$^3J(^{119}Sn,{}^{13}C)$ 37.6]; 139.1; 151.0. ^{119}Sn NMR ($CDCl_3$) δ −27.2. MS m/z (relative intensity): 524 (9) $[M]^+$; 509 (100) $[M\text{-}15]^+$; 494 (22) $[C_{19}H_{26}Sn_2]^+$; 479 (18) $[C_{18}H_{23}Sn_2]^+$; 464 (29) $[C_{17}H_{20}Sn_2]^+$; 449 (17) $[C_{16}H_{17}Sn_2]^+$; 434 (13) $[C_{15}H_{14}Sn_2]^+$; 314 (10) $[C_{15}H_{14}Sn]^+$; 283 (19) $[C_{12}H_{19}Sn]^+$; 165 (23) $[C_3H_9Sn]^+$; 150 (12) $[C_2H_6Sn]^+$; 135 (28) $[CH_3Sn]^+$; 120 (9) [Sn]. Analysis, found : C, 48.62; H, 6.25; calcd for $C_{21}H_{32}Sn_2$ (521.90) : C, 48.33; H, 6.18%.

Synthesis of aryl- and heteroarylpolyboronic acids: reaction of aryl- and heteroaryl organotin compounds with borane in THF

The syntheses by other routes and the physical characteristics of polyarylboronic acids **12**,[16,17] **16**,[18,19] and **17**[20,21] have already been reported. All the reactions were carried out following the same procedure. One experiment is described in detail in order to illustrate the method used.

*Synthesis of 1,4-naphthalenediboronic acid (**12**)*

To a stirred solution of **5** (0.454 g, 1 mmol) in dry THF (10 ml) was added a solution of borane in THF (3 mmol, 2.6 ml of a 1.15 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 3 h. Then the solvent and Me_3SnH (b.p. 59 °C) thus formed were removed under reduced pressure and a white jelly-like residue was obtained. Diethyl ether (10 ml) and water (0.1 ml) were added, the solution was dried over anhydrous magnesium sulfate and the solvent was removed under vacuum. The diboronic acid **12** was obtained (0.177 g, 0.82 mmol, 82%) as a white solid, m.p. >300 °C.[16,17] Using the same technique the following polyboronic acids were obtained.

- *2,7-naphthalenediboronic acid* (**13**)—white solid, m.p. >300 °C, 81%, FTIR (KBr) 3388.9; 1653.4; 1416.9; 1260.3; 1024.9; 814.7; 765.1; 677.8 cm^{-1};
- *3,5-pyridinediboronic acid* (**14**)—yellowish solid, m.p. >300 °C, 79%, FTIR (KBr) 3238.8; 1576.7; 1429.1; 1135.9; 1081.3; 782.6; 704.2 cm^{-1};
- *2,2-di(phenyl-4-boronic acid)propane* (**15**)—white solid, m.p. >300 °C, 82%, FTIR (KBr) 3234.9; 1607.7; 1413.6; 1184.5; 1002.5; 780.5; 652.4 cm^{-1};
- *1, 1′-binaphthyl-2, 2′-diboronic acid* (**16**)—racemic, obtained in 82% yield. FTIR (KBr) 3219.4; 1603.8; 1351.5; 1262.1; 1095.2; 811.7; 714.6 cm^{-1}.

Reaction of aryldiboronic acids 13, 14 and 15 with pinacol: synthesis of pinacol diboronic esters

The following is a representative procedure.

DOI: 10.1002/aoc

*3,5-bis(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (**19**)*

To a stirred suspension of 2,5-pyridinediboronic acid (**14**) (0.2 g, 1.2 mmol) in benzene (4 ml) were added pinacol (0.285 g, 2.4 mmol) and anhydrous magnesium sulfate (1.75 g). The mixture was stirred overnight at room temperature and filtered. The filtrate was concentrated *in vacuo* to afford **19** as an oil. The compound was purified by column chromatography (silicagel 60), **19** being eluted as a colorless oil with hexane : ethyl ether (1 : 1) (0.31 g, 0.94 mmol, 78%). ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 24 H); 7.75 (s, 1H); 8.59 (s, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 24.5; 83.5; 124.6 (br); 135.7; 149.8. MS m/z (relative intensity): 255 (98); 197 (21); 170 (72); 155 (55); 129 (95); 89 (100); 84 (69); 55 (40). Using the same technique, the following polyboronic esters were obtained:

- *2, 2′-[4, 4′-(propane-2,2-diyl)bis(4,1-phenylene)]bis(4,4,5,5-tetramethyl-1,3,2-dioxaboro-lane)* (***20***)—white solid, 75%, m.p.: 220–222 °C. ^{1}H NMR ($CDCl_3$) δ 1.31 (s, 24H); 1.62 (s, 6H); 7.13 [d, 4H, ^{3}J(H,H) 7.9]; 7.45 [d, 4H, ^{3}J(H,H) 7.9]. ^{13}C {^{1}H} NMR ($CDCl_3$) δ 5.2; 30.0; 42.1; 60.1; 62.9; 85.1; 96.9; 146.8; 152.4; C–B signal not observed. MS m/z (relative intensity): 380 (96) $[M\text{-}C_3H_6OB]^+$; 365 (10) $[M\text{-}CH_3]^+$; 294 (64) $[M\text{-}C_6H_{14}]^+$; 280 (50) $[M\text{-}C_{12}H_{24}]^+$; 194 (70) $[M\text{-}C_{12}H_{24}O_4B_2]^+$; 180 (100) $[C_{14}H_{12}]^+$; 85 (30) $[M\text{-}C_{21}H_{25}O_4B_2]^+$; 57 (40) $[M\text{-}C_{24}H_{33}O_3B_2]^+$;
- *2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene* (***18***)—yellowish solid, 71%, m.p.: 135–137 °C. ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 24H); 7.64 [d, 2H, ^{3}J(H,H) 8.4]; 7.79 [d, 2H, ^{3}J(H,H) 8.4]; 8.27 (s, 2H).^{13}C {^{1}H} NMR ($CDCl_3$) δ 25.3; 84.2; 126.1; 128.0; 130.8; 132.6; 137.0 (br); 137.5. MS m/z (relative intensity): 380 (92) $[M]^+$; 365 (24) $[M\text{-}CH_3]^+$; 294 (64) $[M\text{-}C_6H_{14}]^+$; 180 (100) $[M\text{-}C_{12}H_{24}O_2]^+$; 137 (29) $[M\text{-}C_{12}H_{24}O_4B]^+$; 84 (33) $[M\text{-}C_{16}H_{18}O_4B_2]^+$; 57 (40) $[M\text{-}C_{19}H_{25}O_3B_2]^+$.

Suzuki coupling of polyboronic acids with various aryl halides. Synthesis of polycyclic hydrocarbons 21–26

The synthesis by other routes and the physical characteristics of polycyclic hydrocarbons **23**,[22] **24**,[23] **25**[12b] and **26**[24] have already been reported. All the reactions were carried out following the same procedure. One experiment is described in detail in order to illustrate the method used.

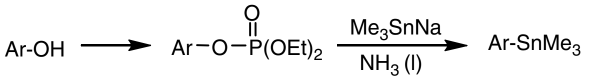
*2,7-Ditolylnaphthalene (**22**)*

p-Iodotoluene (0.15 g, 0.73 mmol), 2,7-naphthyldiboronic acid (**13**) (0.069 g, 0.32 mmol) and triphenylphosphine (0.019 g, 0.072 mmol) were dissolved in 1,2-dimethoxyethane (2 ml). Then, K_2CO_3 (1.9 ml of a 2 M aqueous solution, 0.004 mmol) was added and the mixture was purged with nitrogen. Palladium acetate (0.0039 g, 0.01 mmol) was added and the mixture refluxed for 20 h. The two phases were separated and the aqueous phase was extracted with ethyl acetate (3 × 5 ml). The combined organic phases were washed with water (5 ml) and brine (5 ml), and were dried over anhydrous magnesium sulfate. After evaporation of the solvent, the oily residue was purified by column chromatography (silicagel 60), **22** being eluted with hexane : ethylacetate (9 : 1) (0.073 g, 0.23 mmol, 75%); white solid, m.p. 198–199 °C (EtOH). ^{1}H NMR ($CDCl_3$) δ 2.13 (s, 6H); 6.76 [d, 4H, ^3J(H,H) 8.0]; 7.41 [d, 4H, ^3J(H,H) 8.0]; 7.09–7.40 (m, 6H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 21.6; 126.0; 127.6; 128.4; 130.1; 135.5; 136.2; 136.7; 140.1; 141.2. MS m/z (relative intensity): 309 (16) $[M]^+$; 91 (75) $[M\text{-}C_{17}H_{13}]^+$; 218 (100) $[M\text{-}C_7H_7]^+$; 127 (24) $[M\text{-}C_{14}H_{14}]^+$; 65 (30) $[C_5H_5]^+$. Analysis, found : C, 93.38; H, 6.48; calcd for $C_{16}H_{24}Sn_2$ (453.78) : C, 93.46; H, 6.54%.

Using this technique the following compound was obtained: *1,4-di(tolyl)naphthalene* (***21***)—white solid, 78%, m.p. 184–185 °C (EtOH). ^{1}H NMR ($CDCl_3$) δ 2.19 (s, 6H); 6.82 [d, 4H, ^3J(H,H) 7.8]; 7.31–7.40 (m, 4H); 7.52 [d, 4H, ^3J(H,H) 7.8]; 7.53–7.68 (m, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 20.5; 126.7; 127.4; 128.6; 130.2; 131.0; 135.6; 136.5; 136.7; 141.2. MS m/z (relative intensity): 308 (100) $[M]^+$; 91 (20) $[M\text{-}C_{17}H_{13}]^+$; 218 (30) $[M\text{-}C_7H_7]^+$; 127 (45) $[M\text{-}C_{14}H_{14}]^+$; 65 (30) $[C_5H_5]^+$. Analysis, found : C, 93.34; H, 6.45; calcd for $C_{16}H_{24}Sn_2$ (453.78) : C, 93.46; H, 6.54%.

RESULTS AND DISCUSSION

Phenols are easily converted into the corresponding aryl diethyl phosphate esters (arylDEP) in very high yields (85–90%).[14] In previous studies it has been shown that the diethyl phosphate group acts as a nucleofuge in the reaction of arylDEP esters with trimethyl- and triphenyltin anions in liquid ammonia, under irradiation (see general part in Experimental), leading to the corresponding aryl trialkylstannyl substituted compounds via an $S_{RN}1$ mechanism [equation (1)].[11–13]

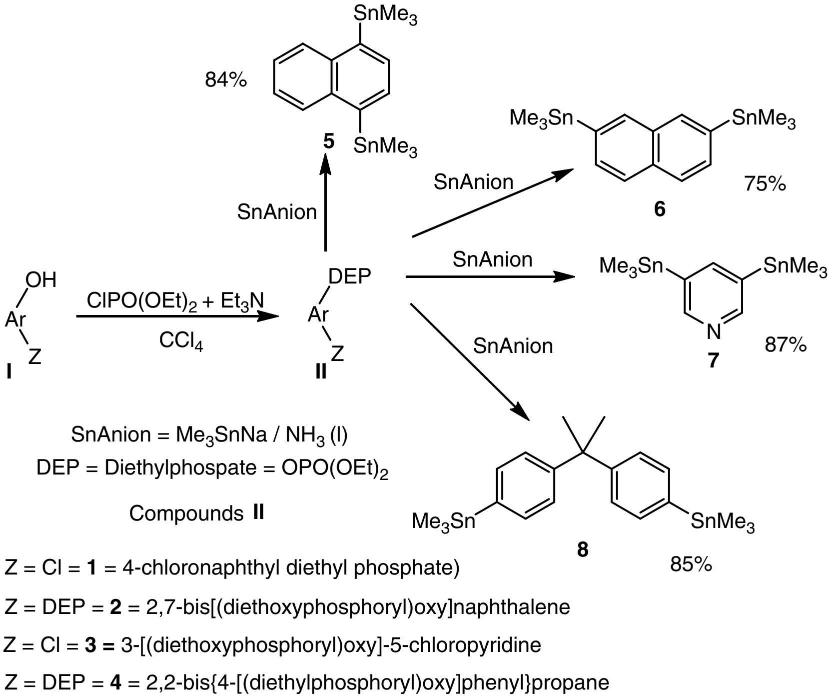


$$\text{Ar-OH} \longrightarrow \text{Ar}{-}\text{O}{-}\overset{\overset{\text{O}}{\|}}{\text{P}}(\text{OEt})_2 \xrightarrow[\text{NH}_3\,(\text{l})]{\text{Me}_3\text{SnNa}} \text{Ar-SnMe}_3 \qquad (1)$$

$$\text{Ar-SnR}_3 + \text{BH}_3 \xrightarrow{\text{THF}} \text{Ar-B(OH)}_2 + \text{R}_3\text{SnH} \qquad (2)$$

R = Me, n-Bu

Taking into account both the wide variety of phenols available and their relative low cost, we considered that this two-step synthesis should be the one to choose in order to obtain the aryl- and heteroaryl trialkylstannyl substituted compounds needed for the study of their reactions with borane in THF. In order to explore the scope of this route, we also considered it of interest to carry out the synthesis of some new aryl bis(diethylphosphates) and chloroaryl diethyl phosphates as well as the new aryl bistriorganotin compounds **6** and **8**, as shown in Fig. 1. The reaction of esters **1**–**4** with sodium trimethylstannide (Me_3SnNa) in liquid ammonia led to the corresponding arylbistrimethyltin compounds **5**–**8** with an average 82% yield.



SnAnion = Me_3SnNa / NH_3 (l)
DEP = Diethylphospate = $OPO(OEt)_2$

Compounds **II**

Z = Cl = **1** = 4-chloronaphthyl diethyl phosphate)
Z = DEP = **2** = 2,7-bis[(diethoxyphosphoryl)oxy]naphthalene
Z = Cl = **3** = 3-[(diethoxyphosphoryl)oxy]-5-chloropyridine
Z = DEP = **4** = 2,2-bis{4-[(diethylphosphoryl)oxy]phenyl}propane

Figure 1. Two-steps synthesis of arylbis(trimethyltin) compounds starting from phenols.

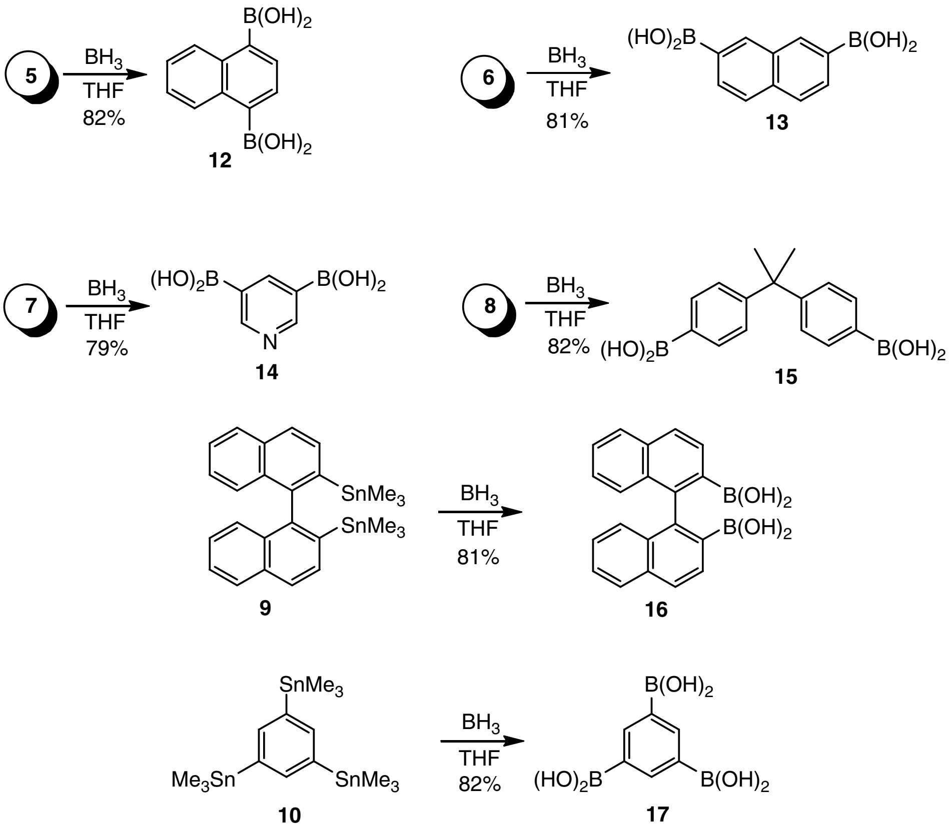


Figure 2. Synthesis of arylpolyboronic acids via transmetallations between arylpoly(trimethyltin) compounds and borane in THF.

DOI: 10.1002/aoc

The obtained results confirm that the conversion of phenols into the corresponding aryl diethyl phosphates followed by the $S_{RN}1$ displacement with organotin anions is an excellent and very convenient method for the synthesis of aryldistannanes. The main advantages of the synthesis of arylstannanes following this method is that the two operational steps, phenol-ester-organotin, can be performed at moderate temperature, so it should be possible to use the method in the synthesis of thermally labile molecules, and also that the aromatic ring could contain various substituents. An additional attractive feature of this method is that the starting phenols are readily available and more economical than other starting materials.

Compounds **5–8,** as well as arylpolyorganotins **9** and **10** obtained following the same protocol, were made to react with borane in THF. As shown in Fig. 2, these reactions led to the corresponding arylpolyboronic acids in good yields.

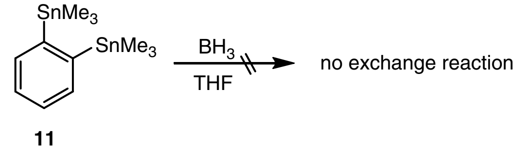


Figure 3. o-Bis(trimethyltin)benzene fails to react with borane.

The arylboronic acids were obtained pure and uncontaminated by organotin residues and by other organic and inorganic boron derivatives as well as free of organic halides.

Under the same reaction conditions, bis(trimethylstannyl) benzene (**11**) does not react with borane in THF: only starting compound **11** was recovered (Fig. 3). This might be connected with the higher steric hindrance that would appear when the two trimethyltin moieties were replaced by two boron substituents in *ortho*.

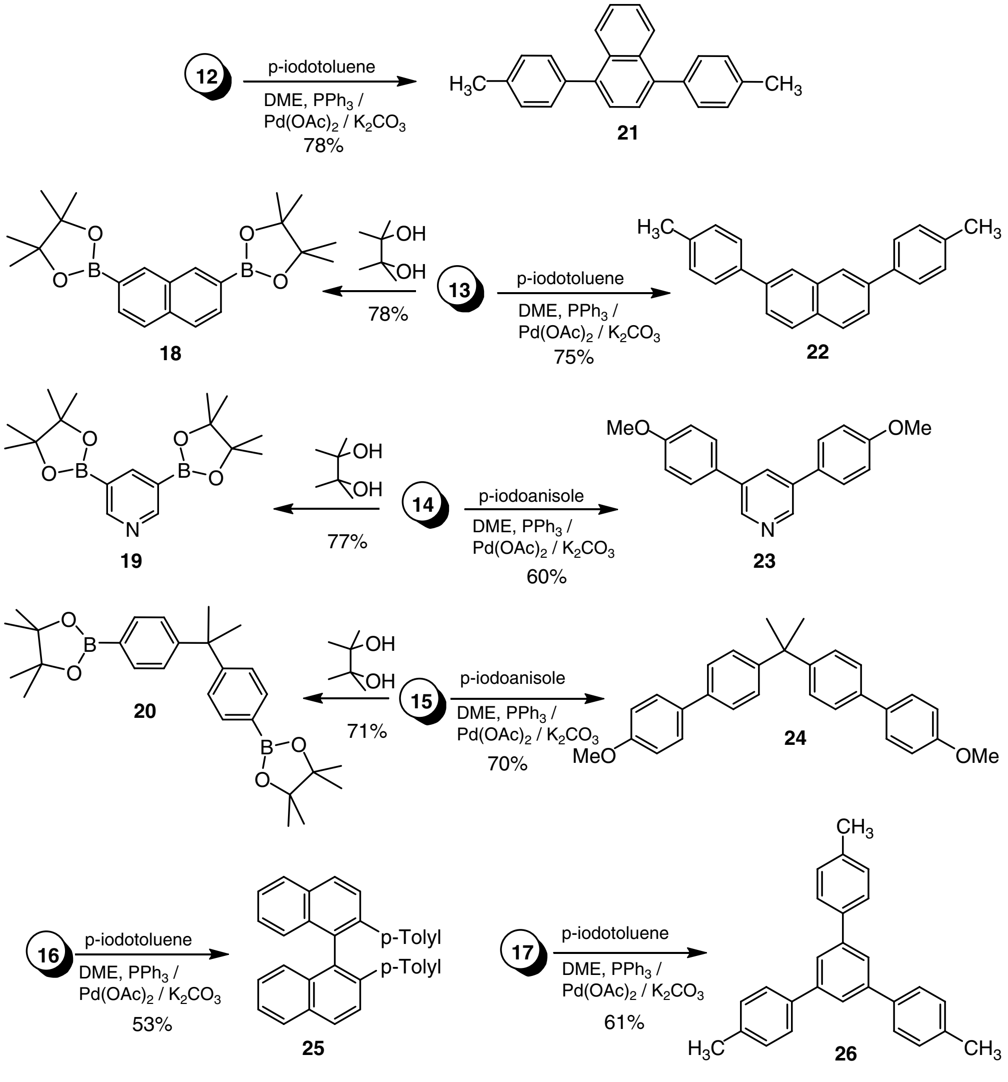


Figure 4. Synthesis of pinacol boronic esters and aromatic polycyclic hydrocarbons.

DOI: 10.1002/aoc

It should be noted that we could not obtain good microanalyses of the new 2,7-naphthalenediboronic acid (**13**), 3,5-pyridinediboronic acid (**14**) and 2,2-di(phenyl-4-boronic acid)propane (**15**). This is not surprising, because it has been reported that boronic acids in general present a host of difficulties with regard to analysis, the principal one being their spontaneous condensation to boroxines to varying degrees.[6]

In order to confirm, at least indirectly, the structure of the diboronic acids **13–15**, we first obtained the corresponding pinacol diboronic esters **18–20** (Fig. 4), whose ^{1}H and ^{13}C NMR spectra confirmed the structure of the starting diboronic acids **13–15**.

We then carried out a study on the synthesis of various terphenyls through double and triple Suzuki couplings catalyzed by palladium acetate between arylpolyboronic acids **12-17** and various aryl halides, as shown in Fig. 4. These reactions led to a series of terphenyls in yields of around 75% (Fig. 4). They also enabled us to confirm the structures of diboronic acids **13–15**.

The physical characteristics of compounds **23**,[22] **24**,[23] **25**[19] and **26**[24] were in agreement with those found in the literature. The new 1,4-ditolylnaphthalene (**21**) and 2,7-ditolylnaphthalene (**22**) were characterized by IR, mass and NMR spectra.

These studies confirm that the transmetalation of poly(trimethylstannyl)aromatic and heteroaromatic compounds with borane in THF is an excellent method for the synthesis of pure, valuable polyboronic acids, and also that the double and triple Suzuki couplings could be performed with good yields.

Acknowledgments

This work was been sponsored by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET, Argentina), the Universidad Nacional del Sur (Bahía Blanca, Argentina) and the Comisión de Investigaciones Científicas, Provincia de Buenos Aires, La Plata, (CIC, Argentina). Fellowships from CONICET (to G.E.S. and P.M.F.) and a travel grant to one of us (J.C.P.) from the Alexander von Humboldt Foundation (Germany) are gratefully acknowledged.

REFERENCES

1. Suzuki A. *Metal-catalyzed Cross-coupling Reactions*, Diederich F, Stang PJ (eds). Wiley-VCH: Weinheim, 1997; Chapter 2.
2. Miller TM, Neenan TX, Zayas R, Bair HE. *J. Am. Chem. Soc.* 1992; **114**: 1018.
3. Tour JM, Lamba JJS. *J. Am. Chem. Soc.* 1993; **115**: 4935.
4. Morgan AB, Jurs JL, Tour JM. *J. Appl. Polym. Sci*, 2000; **76**: 1257.
5. Nielsen DR, McEwen WE. *J. Am. Chem. Soc.* 1957; **79**: 3081.
6. Todd MH, Balasubramanian S, Abell C. *Tetrahedron Lett.* 1997; **38**: 6781.
7. Mandolesi SD, Vaillard SE, Podestá JC, Rossi RA. *Organometallics*, 2002; **21**: 4886.
8. Yammal CC, Podestá JC, Rossi RA. *J. Org. Chem.*, 1992; **57**: 5720.
9. Corsico EF, Rossi RA. *Synlett*, 2000; 227.
10. Chopa AB, Lockhart MT, Silbestri G. *Organometallics* 2001; **20**: 3358.
11. Chopa AB, Lockhart MT, Silbestri G. *Organometallics* 2000; **19**: 2249.
12. Chopa AB, Lockhart MT, Dorn VB. *Organometallics* 2002; **21**: 1425.
13. Chopa AB, Lockhart MT, Silbestri G. *Organometallics* 2002; **21**: 5874.
14. Kenner GW, Williams NR. *J. Chem. Soc.* 1955; 522.
15. Kaim W, Tesmann H, Bock H. *Chem. Ber.* 1980; **113**: 3221.
16. Allen LM, Roscoe CW. *J. Pharm. Sci.* 1969; **58**: 368.
17. Zhang F-J, Cortez C, Harvey RG. *J. Org. Chem.* 2000; **65**: 3952.
18. Schilling B, Kaufmann D. *Eur. J. Org. Chem.* 1998; 701.
19. Kasak P, Brath H, Dobovska M, Juricek M, Putala M. *Tetrahedron Lett.* 2004; **45**: 791.
20. Morgan A, Jurs J, Tour J. *Polym. Preprints (Am. Chem. Soc., Div. Polym. Chem.)* 1999; **40**: 2, 553.
21. Morgan A, Jurs J, Tour J. *J. Appl. Polym. Sci.* 2000; **76**: 8, 1257.
22. Balasubrahmanyam B, Jeyashri I, Namboothiri N. *Tetrahedron* 1994; **50**: 8127.
23. Boyles D, Filipova T, Bendler J, Longbrake G, Reams J. *Macromolecules* 2005; **38**: 3622.
24. Jiang J, Chen M. *J. Org. Chem.* 2001; **66**: 3627.

DOI: 10.1002/aoc