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Synthesis of *trans*-arylvinylboronates via a palladium catalysed cross-coupling of a vinylboronate ester with aryl halides

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Abstract

Vinylboronate **1**, protected as its pinacol ester, can be cross-coupled with aryl halides in the presence of palladium(0) to give the styrylboronate **2** as the major or exclusive product under optimized reaction conditions. The styrylboronate Heck products **2** are obtained with higher yields when aryl iodides rather than aryl bromides are used. Heteroaromatic halides are only reactive when silver(I) salts are added to the reaction mixture.

Key words: Palladium; Aryl Halides; Coupling; Boronate; Vinyl

1. Introduction

The formation of new asymmetrical carbon–carbon bonds can be readily accomplished using a wide range of palladium-catalysed cross-coupling procedures [1]. One of these processes which has received a great deal of attention for the synthesis of a wide range of carbon frameworks involves the coupling of an organometal derivative with an alkyl or aryl halide, organoboron derivatives being especially useful [2]. The main reasons for the use of organoboron reagents for these coupling reactions are that (a) organoboron compounds can be readily prepared by a variety of convenient procedures and (b) the coupling reactions tend to be high yielding, with few side reactions, and to occur under relatively mild conditions. These features attracted our attention for application in the area of the synthesis of polyenes.

Recently we reported [3] our early experiments to develop new cross-coupling procedures, which would produce products which retained a reactive functional group. We found that the reaction of an alkenylboronate, such as **1**, which is a stable boronate ester, can react by either the Heck [4*] or the Suzuki [5] pathway (Scheme 1). This would afford either arylvinylboronate **2** or styrene **3**, depending upon whether the palladium(0) added across the alkene or inserted into the C–B bond of **1** (*see below*). Our intention was to develop conditions that would allow the Heck reaction product to be produced at the expense of the Suzuki product. Under these conditions, the vinylboronate **1** could then be considered as a *trans*-vinyldianion equivalent, since the product from a Heck coupling (*i.e.* **2**) would retain a boronate moiety for a further coupling reaction.

In this paper we report the full details of our work on the coupling of vinylboronate ester **1** to various aryl halides, on the conditions which affect the selectivity of the Heck *vs.* Suzuki processes and on the best reaction conditions that we have discovered so far; we also discuss the possible mechanisms involved.

2. Results and Discussion

In our initial communication [3] we reported the results of the reaction of vinylboronate **1** [6] with a range of aryl halides (electron-rich and electron deficient bromides and iodides), solvents (polar *vs.* nonpolar), bases (amines and alkoxides), palladium sources (palladium(II) acetate and tetrakistriphenylphosphinylpalladium(0)), palladium ligands (triphenylphosphine,

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* A reference number with an asterisk indicates a note in the list of references.

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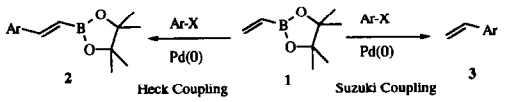
1,10-phenanthroline or trialkylamine) and reaction temperatures (40–110°C) to see whether we could find optimum conditions favouring the Heck over the Suzuki reaction. It was clear at that stage that a single set of conditions that gave reasonable yields and selectivity for the Heck products **2** had not been found. Indeed, different halides seemed to require subtly different reaction conditions. We have now considerably ex-

TABLE 1. Results

Number	Aryl halide	Method [a]	Temperature (°C)	Time (h)	Conversion (%) [b]	2:3 ratio [c]	Yield 2 [d,e]
1	Iodobenzene	A	65	4	100	> 95:5	66 [f]
2	Iodobenzene	B	80	40	> 90	87:13	32 [g]
3a	Iodobenzene	B [h]	80	3	20	< 5:95	< 1 [i]
3b	Iodobenzene	B [h]	80	9	100	100:0	100 [i]
4	2-Bromoanisole	A	80	18	48	50:50	12 [g]
5	2-Iodoanisole	C	45	6	53	33:67	17 [i]
6	4-Bromoanisole	A [j]	80	20	30	0:100	NA
7	4-Bromoanisole	A	80	24	100	55:45	55 [i]
8	4-Bromoanisole	B	80	24	> 95	69:31	24 [g] (6 [k])
9	4-Iodoanisole	A	65	6	59	< 10:90	NA
10	4-Iodoanisole	A [l]	110	4.5	100	80:20	50 [i]
11	4-Bromotoluene	A	65	24	32	20:80	7 [i]
12	4-Bromotoluene	A [m]	110	70	64	80:20	51 [g]
13	4-Bromotoluene	B	80	70	23	17:83	4 [i]
14	4-Iodotoluene	A	65	6	49	43:57	21 [i]
15	4-Iodotoluene	A [l]	110	4	97	100:0	69 [g]
16	4-Iodotoluene	D	65	8	58	75:25	20 [g]
17	4-Iodotoluene	D	45	6	40	100:0	40 [i]
18	4-Iodotoluene	C	45–65	110	30	< 10:90	NA
19	4-Iodotoluene	C [n]	60	26	100	0:100	NA
20	Methyl 2-iodobenzoate	D	65	6	55	60:40	8 [g]
21	Methyl 2-iodobenzoate	C	45	6	100	0:100	NA
22	Methyl 2-iodobenzoate	A [l]	110	18	100	87:13	58 [g]
23	4-Bromobenzaldehyde	D	65	24	70	75:25	24 [g]
24	4-Bromonitrobenzene	A	80	20	35	17:83	6 [i]
25	4-Bromonitrobenzene	A [l]	110	71	63	60:40	38 [i]
26	4-Bromonitrobenzene	A [m]	110	67	> 90	35:65	47 [g,o]
27	1-Bromonaphthalene	A	110	24	100	62:38	57 [g]
28	1-Bromonaphthalene	D	65	72	40	74:26	30 [i]
29	1-Bromonapthalene	A [m]	110	95	> 90	87:13	48 [g]
30	1,8-Diiodonaphthalene	A [l]	110	48	100	NA	77 [g]
31	1,8-Diiodonaphthalene	A	65	24	100	NA	14 [g]
32	1-Iodothiophene	A [m]	65	48	< 5	0:100	NA
33	1-Iodothiophene	E	65	6	> 95	92:8	46 [g]
34	1-Bromopyridine	A [m]	65	96	0	NA	NA
35	1-Bromopyridine	E	65	144	< 5	NA	< 5 [k]

NA, not available.
[a] See Section 3.
[b] Conversion was estimated relative to consumed aryl halide by 200 MHz ^{1}H NMR.
[c] 2:3 ratio of products was estimated from the crude 200 MHz ^{1}H NMR spectrum.
[d] Yields are quoted relative to aryl halide used and are unoptimized.
[e] All compounds had satisfactory spectroscopic and analytical properties.
[f] Isolated yield after distillation.
[g] Isolated yield after silica gel chromatography.
[h] Method as B, but tributylamine used instead of triethylamine.
[i] NMR yield.
[j] Method as A, but THF replaces acetonitrile.
[k] Styrylboronate side product.
[l] Method as A, but tributylamine and toluene used instead of triethylamine and acetonitrile, with 2.5 mol% Pd catalyst.
[m] Method as A, but with tributylamine, toluene, 5 mol% Pd catalyst, and 10 mol% triphenylphosphine.
[n] Method as C, but using triphenylphosphine instead of 1,10-phenanthroline.
[o] Combined yield of mixture; see Section 3.
[p] Mixture of at least four products by TLC and ^{1}H NMR.



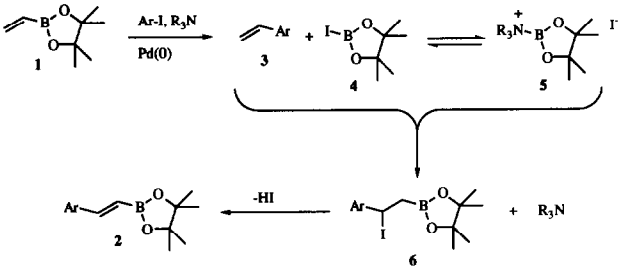
Scheme 1.

tended the range of reaction conditions tested, in the hope of finding a general procedure that will work for all aryl halides. The combined set of results are summarised in Table 1, which shows our original results and those that give the highest yields of Heck products of type **2**.

As may be surmised from the number of results shown in Table 1, it proved very difficult to find a single set of reaction conditions that provided only the Heck products for all aryl halides. However, one set of conditions did seem to be generally the most satisfactory and several observations are worth noting.

Initially [3] it seemed that reactions conducted at lower temperatures (45 *vs.* 65°C) favoured the Heck products **2** over the Suzuki products **3** (see for example Table 1, numbers 16 and 17), suggesting that the Heck products **2** may be kinetically preferred (see below). However, upon further examination, some odd results were obtained, suggesting that an alternative mode of reaction may be operating in these coupling processes. The best example of this is provided by Table 1, number 3a and 3b, which refer to a single reaction that was carefully monitored over a period of time. After 3 h, the reaction of iodobenzene at 80°C (using tetrakistriphenylphosphinylpalladium(0) as catalyst) showed only approximately 20% conversion of the halide, and, more importantly, had given only Suzuki product **3** (by ^{1}H NMR). However, after 9 h, the reaction had gone to completion, and there was no sign of any Suzuki product **3** present or of any insoluble polymer derived therefrom. Instead the reaction had cleanly produced Heck product **2**. This observation prompted us to propose that, together with the effect of kinetic *vs.* thermodynamic control in determining the ratio of Heck and Suzuki products, there is an effect arising from the operation of an additional process. It seemed likely that the styrene products **3** resulting from a Suzuki-type coupling may be reacting with the iodoborate byproducts **4** or **5** *i.e.* by an iodoboration of the styrene (affording **6**), followed by elimination to give the Heck products **2**, as shown in Scheme 2.

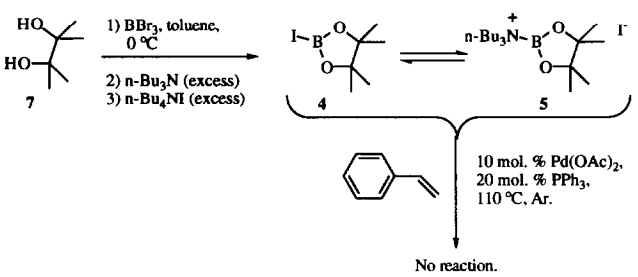
We attempted to test this theory by preparing iodoborate **4** (or **5**) *in situ*, by reaction of anhydrous pinacol **7** with tribromoborane, followed by addition of excess tetrabutylammonium iodide and tributylamine (Scheme 3). Addition of styrene to this mixture produced no reaction, including polymerization and, when palladium(II) acetate (up to 10 mol.%) and triphenylphosphine (up to 20 mol.%) were added and when the mixture was heated at 110°C for up to 20 h, still no reaction took place. Although this does not necessarily prove that the reaction outlined in Scheme 2 does not operate, it strongly suggests that an alternative explanation for the change in product ratios over time is required.



Scheme 2.

It seems that the source of palladium(0) used in the reaction (as indicated in Table 1) played only a minimal part in the reaction, since palladium acetate gave similar results to tetrakistriphenylphosphinylpalladium (0), but the use of phenanthroline [7] as ligand tended to give greater selectivity for the Heck product **2**. Tributylamine was slightly superior in most of the reactions to triethylamine in that the conversions were very similar but the Heck products **2** were generally obtained with higher selectivity, especially when the tributylamine was used in toluene at 110°C, as in Table 1, numbers 10, 12, 15, 22, 25 and 26. The high yield of the double Heck product **8** from 1,8-diidonaphthalene in the presence of tributylamine in toluene (Table 1, number 30) is especially note worthy in this context, since the corresponding reaction in the presence of triethylamine in acetonitrile gave a mixture of all possible products, with **8** being isolated with only 14% yield after chromatography (Table 1, number 31).

It is also noteworthy that, in the case of 4-bromoanisole (Table 1, number 8) exchange of the aryl groups on the phosphine ligands occurs. Instead of isolating the expected Heck product (*i.e.* **9**) and Suzuki product (*i.e.* **10**), we obtained a Heck-derived product

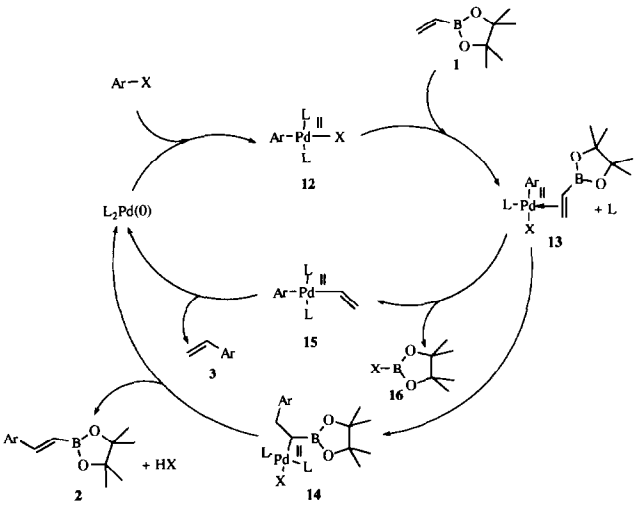


Scheme 3.

without the methoxy group, *i.e.* **11**. This type of exchange of less-electron-donating aryl groups on phosphorus for more-electron-donating groups in the presence of tetrakis(triphenylphosphinyl)palladium(0) has been reported previously [8]. The same product **11** was also isolated (with less than 5% yield) as the only product from the attempted reaction of bromopyridine (Table 1, number 34) with vinylboronate **1**. In this case, the small amount of styrene **11** produced can be explained in terms of the extremely long reaction time and the use of triphenylphosphine as the aryl source.

Attempts were made to carry out these coupling reactions with heterocyclic aromatic halides (Table 1, numbers 32–34). These halides were unreactive under the usually successful conditions (method A^m), but iodothiophene did react cleanly to give the corresponding Heck product when silver(I) acetate was added to the reaction mixture (Table 1, number 33). 2-Bromopyridine was completely unreactive under these conditions (Table 1, number 34).

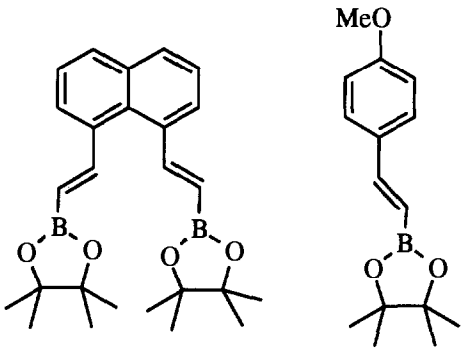
The most important conclusions to be drawn from Table 1 are that it was possible to obtain the Heck products **2** as the major product in virtually all cases by using the higher reaction temperature (in toluene) and preferably the more reactive aryl iodides. Procedures for the best conditions found for each aryl halide are reported in Section 3 together with the general methods.



Scheme 4.

Our recent results still suggest that the observed reaction products are determined by a similar route to that previously discussed [3], *i.e* through an intermediate palladium complex such as **13** (Scheme 4) which can either add across the C=C bond to give **14** or insert into the C–B bond to give **15**. However, it now seems likely that superimposed upon this reaction scheme (Scheme 4) there is another process which drives the reaction (albeit slowly) to completion. This mode of reaction appears when the higher reaction temperature (110°C) and prolonged reaction times are used. Despite our inability to show that the most likely process responsible for these results is a haloboration–elimination sequence, it is possible that the byproduct from the Suzuki pathway, *i.e.* borate derivative **16** (or some derivative thereof), is involved in a reaction; it remains more likely that the reactive aryl iodides react with vinylboronate **1** by a standard Heck-type mechanism (Scheme 4).

In summary, vinylboronates undergo both Suzuki and Heck cross-coupling, and reasonable to high selectivity for the Heck product is generally possible. The product distributions are strongly dependent upon the reaction conditions, but use of the aryl iodide under more forcing conditions (110°C) gives reproducible results. Heterocyclic aromatic halides are less reactive, but addition of a silver(I) salt to rings about formation of the Heck product from 2-iodo thiophene. Further investigations of these coupling reactions, aimed particularly at expanding the range of utility of the couplings, are in progress.



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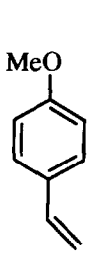

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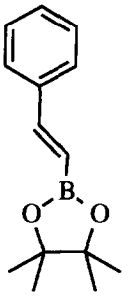

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3. Experimental details

Dichloromethane was distilled from calcium hydride. Light petroleum refers to the fraction boiling at 40–60°C. All solvents were dried before use; tetrahydrofuran (THF) was distilled under argon from benzophenone and sodium, and toluene and acetonitrile were distilled from calcium hydride. Tri-*n*-butylamine and triethylamine were purchased from Aldrich or Janssen and stored over potassium hydroxide pellets. Vinylmagnesium bromide (1 M solution in THF), trimethylborate and pinacol were purchased from Aldrich. Tetrakis(triphenylphosphinyl)palladium(0), palladium(II) acetate, phenanthroline monohydrate and triphenylphosphine were used as purchased from Aldrich or Janssen but were kept sealed under argon. The vinylboronate **1** was prepared by a similar procedure to that previously reported [6,9].

Thin layer chromatography (TLC) was performed on Merck plastic or aluminium sheets coated with silica gel 60 F_{254} (Art 5735); the chromatograms were initially examined under UV light and then developed either with iodine vapour or with an ethanolic anisaldehyde (1.0%) solution containing sulphuric acid (9%) used as a spray and visualized by heating with a heat gun. Column chromatography was carried out under medium pressure or under gravity, on Merck Kieselgel H (type 60).

All anhydrous low temperature reactions were carried out in glassware which had been dried by storage in a glass oven at 140°C and cooled under a stream of argon. All reactions were carried out under argon. All organic extracts were dried over anhydrous magnesium sulphate or anhydrous sodium sulphate. Evaporations were carried out with a Buchi rotary evaporator or Buchi cold-finger rotary evaporator, followed by evaporation under high vacuum (typically at approximately 2 Torr Hg). Kugelruhr distillations were carried out with a Buchi GKR-51 Kugelruhr apparatus. Melting points (m.p.s) were determined with an electrothermal melting-point apparatus. ^{1}H spectra were recorded in $CDCl_3$ solutions at 200 or 300 MHz on a Bruker AC200 or AC300 NMR spectrometer. IR spectra were recorded on a Perkin–Elmer spectrometer 783 equipped with a PE600 data station, and UV spectra were recorded on a Perkin–Elmer 115 spectrometer. Electron impact (EI) (70 eV) and chemical ionization (CI) spectra were obtained with a Kratos MS25 spectrometry. Fast atom bombardment (FAB) spectra were obtained with a Kratos MS50 spectrometry with an *m*-nitrobenzyl-alcohol as matrix and accurate mass determinations were carried out on a Kratos Concept IS spectrometer. Microanalyses were performed with a Carlo–Erba 1106 elemental analyser.

The general conditions for the methods used the results of which are reported are as follows: method A, $Pd(OAc)_2$ (2.5 mol.%), PPh_3 (5 mol.%), aryl halide (1 equivalent), vinylboronate **1** (1.2 equivalent), Et_3N (1.2 equivalent), MeCN, Ar, Δ; method B, $Pd(PPh_3)_4$ (5 mol.%), aryl halide (1 equivalent), vinylboronate **1** (1.2 equivalent), Et_3N (1.2 equivalent), MeCN, Ar, Δ; method C, $Pd(OAc)_2$ (5 mol.%), phenanthroline (5 mol.%), aryl halide (1 equivalent), vinylboronate **1** (3 equivalents), ^{t}BuOK (3 equivalents), MeCN, Ar, Δ; method D, $Pd(OAc)_2$ (5 mol.%), phenanthroline (5 mol.%), aryl halide (1 equivalent), vinylboronate **1** (1.2 equivalents), Et_3N (2 equivalents), MeCN, Ar, Δ; method E, $Pd(OAc)_2$ (5 mol.%), PPh_3 (10 mol.%), aryl halide (1 equivalent), vinylboronate **1** (1.2 equivalent), *n*-Bu_3N (2 equivalents), AgOAc (1 equivalent), toluene, Ar, Δ.

3.1. Preparation of styrylboronate (Table 1, number 2)

Iodobenzene (0.30 ml, 2.71 mmol) was added to a solution of tetrakis(triphenylphosphine)palladium(0) (0.079 g, 0.08 mmol) in dry acetonitrile (5 ml) under argon. Triethylamine (0.45 ml, 3.24 mmol) and vinylboronate **1** (0.500 g, 3.24 mmol) were added; then the mixture was stirred at 60°C for 48 h, cooled, diluted with dichloromethane (100 ml) and shaken successively with 10% hydrochloric acid, water and saturated aqueous sodium chloride. Drying, filtration and evaporation of the organic layer gave a pale-yellow oil, which was purified by silica gel chromatography (hexane : diethyl ether, 95 : 5, as eluant to give the Heck product as a colourless oil (0.235 g; 32%). IR, ^{1}H NMR and mass spectra were identical with those reported previously [10].

3.2. Preparation of o-methoxystyrylboronate (Table 1, number 4)

o-Bromoanisole (0.67 ml, 5.41 mmol) was added to a solution of palladium(II) acetate (0.033 g, 0.13 mmol) and triphenylphosphine (0.071 g, 0.27 mmol) in dry acetonitrile (8 ml) under argon. Triethylamine (0.91 ml, 6.49 mmol) and vinylboronate **1** (1.00 g, 6.49 mmol) were added; then the mixture was stirred at 80°C for 18 h, diluted with ethyl acetate (100 ml) and shaken successively with, 10% hydrochloric acid, water and saturated aqueous sodium chloride solution. Drying, filtration and evaporation of the organic layer gave a dark-brown oil, which was purified by silica gel chromatography (hexane : diethyl ether, 90 : 10, then 80 : 20, as eluant) to give the Heck product as a pale-yellow oil (0.169 g, 12%). IR (film): ν_{max} *inter alia* 1620 (C=C) cm^{-1}. ^{1}H NMR (200 MHz): δ 1.31 (12H, s, 2 × C.Me_2), 3.85 (3H, s, O.Me), 6.18 (1H, d, J = 18.6 Hz, Ar.CH:C*H*.B), 6.85–6.97 (2H, m, ArHs), 7.22–7.28 (1H,

m, ArH), 7.55 (1H, dd, $J = 7.6$ and 1.7 Hz, ArH), 7.77 (1H, d, $J = 18.6$ Hz, Ar.C*H*:CH.B). Mass spectroscopy (MS) (EI): m/z 260 (54%, M^+), 245 (7%, $M^+ - CH_3$), 187 (100%, $M^+ - C_4H_9O$). Accurate MS. Found: m/z 260.1570. $C_{15}H_{21}BO_3$ calc.: m/z 260.1584.

3.3. Preparation of p-methoxystyrylboronate (Table 1, number 10)

p-Iodoanisole (0.630 g, 2.71 mmol) was dissolved in a solution of palladium(II) acetate (0.008 g, 0.03 mmol) and triphenylphosphine (0.021 g, 0.08 mmol) in dry toluene (8 ml) under argon. Tri-*n*-butylamine (1.30 ml, 5.41 mmol) and vinylboronate **1** (0.750 g, 4.87 mmol) were added; then the reaction was stirred at 111°C for 5 h, diluted with diethyl ether (50 ml) and shaken successively with 10% hydrochloric acid, water and saturated aqueous sodium chloride. Drying, filtration and evaporation gave a dark-yellow oil, which was purified by silica gel chromatography (hexane : diethyl ether, 95 : 5, then 90 : 10, as eluant) to give the Heck product as a pale-yellow solid (0.348 g; 50%); m.p., 53–54°C. IR (KBr disc): ν_{max} *inter alia* 16.25 (C=C) cm^{-1}. ^1H NMR (200 MHz): δ 1.31 (12H, s, $2 \times C.Me_2$), 3.81 (3H, s, O.Me), 6.01 (1H, d, $J = 18.5$ Hz, Ar.CH:C*H*.B), 6.86 (2H, dd, $J = 6.8$ Hz, 2.0 Hz, ArH's), 7.35 (1H, d, $J = 18.5$ Hz, Ar.C*H*:CH.B), 7.43 (2H, dd, $J = 6.8$ and 2.0 Hz, ArHs). MS (FAB): m/z 260 (100%, M^+), 245 (29%, M^+-CH_3). Accurate MS. Found: m/z 261.1648. $C_{15}H_{21}BO_3 + H$ calc.: m/z 261.1662. Anal. Found: C, 69.0; H, 8.4. $C_{15}H_{21}BO_3$ calc.: C, 69.3; H, 8.2%.

3.4. Preparation of p-methylstyrylboronate (Table 1, number 15)

This compound was prepared by the same method described for *p*-methoxystyrylboronate above but from *p*-iodotoluene (0.591 g, 2.71 mmol), palladium(II) acetate (0.008 g, 0.03 mmol), triphenylphosphine (0.021 g, 0.08 mmol), tri-*n*-butylamine (1.30 ml, 5.41 mmol), vinylboronate **1** (0.750 g, 4.87 mmol) and dry toluene (8 ml). Purification by silica gel chromatography (hexane : ethyl acetate, 97.5 : 2.5, then 95 : 5 as eluant) gave the Heck product as a pale-yellow solid (0.458 g, 69%); m.p., 58–59°C. IR (KBr disc): ν_{max} *inter alia* 1630 (C=C) cm^{-1}. ^1H NMR (200 MHz): δ 1.31 (12H, s, $2 \times C.Me_2$), 2.34 (3H, s, Ar.*Me*), 6.11 (1H, d, $J = 18.5$ Hz, Ar.CH:C*H*.B), 7.14 (2H, d, $J = 8.1$ Hz, ArHs), 7.37 (1H, d, $J = 18.5$ Hz, Ar.C*H*:CH.B), 7.38 (2H, d, $J = 8.1$ Hz, ArHs). MS (EI): m/z 244 (92%, M^+), 229 (15%, $M^+ - CH_3$), 144 (100%, $M^+ - C_6H_{12}O$). Accurate MS. Found: m/z 244.1638. $C_{15}H_{21}O_2B$ calc.: m/z 244.1635.

3.5. Preparation of o-carboxymethylstyrylboronate (Table 1, number 22)

This compound was prepared by the method described for *p*-methoxystyrylboronate above but from methyl 2-iodobenzoate (0.40 ml, 2.71 mmol), palladium(II) acetate (0.008 g, 0.03 mmol), triphenylphosphine (0.021 g, 0.08 mmol), tri-*n*-butylamine (1.30 ml, 5.41 mmol), vinyl boronate **1** (1.000 g, 6.49 mmol) and dry toluene (8 ml). Purification by silica gel chromatography (dichloromethane as eluant) gave the Heck product as a pale-brown oil (0.450 g; 58%). IR (film): ν_{max} *inter alia* 1725 (C=O), 1625 (C=C) cm^{-1}. ^1H NMR (200 MHz): δ 1.31 (12H, s, $2 \times C.Me_2$), 3.91 (3H, s, CO_2Me), 6.07 (1H, d, $J = 18.3$ Hz, Ar.CH:C*H*.B), 7.30–7.38 (1H, m, ArH), 7.45–7.53 (1H, m, ArH), 7.64 (1H, d, $J = 7.8$ Hz, ArH), 7.86 (1H, dd, $J = 7.8$ and 1.4 Hz, Ar), 8.08 (1H, d, $J = 18.3$ Hz, Ar.C*H*:CH.B). MS (FAB): m/z 289 (63%, $M^+ + H$), 273 (30%, $M^+ - CH_3$), 189 (42%, $M^+ - C_6H_{11}O$), 145 (100%, $M^+ - C_7H_{16}BO_2$). Accurate MS. Found: m/z 289.1616 $C_{16}H_{21}O_4B + H$ calc.: m/z 289.1611. Anal. Found: C, 66.4; H, 7.7 $C_{16}H_{21}BO_4$ calc.: C, 66.7; H, 7.4%.

3.6. Preparation of p-formylstyrylboronate (Table 1, number 23)

p-Bromobenzaldehyde (0.500 g, 2.71 mmol) was added to a solution of palladium(II) acetate (0.033 mg, 0.16 mmol) and 1,10-phenanthroline monohydrate (0.027 g, 0.16 mmol) in dry acetonitrile (8 ml), under argon. Triethylamine (0.75 ml, 5.41 mmol) and vinylboronate **1** (0.500 g, 3.25 mmol) were added; then the mixture was stirred at 60°C for 21 h, diluted with diethyl ether (70 ml), washed successively with 10% hydrochloric acid, water, and aqueous saturated aqueous sodium chloride. Drying, filtration and evaporation gave a brown oil, which was purified by silica gel chromatography (dichloromethane as eluant) to give the Heck product as a pale-yellow solid (0.170 g, 24%); m.p., 104–105°C. IR (KBr disc): ν_{max} *inter alia* 1690 (C=O), 1625 (C=C) cm^{-1}. ^1H NMR (200 MHz): δ 1.32 (12H, s, $2 \times C.Me_2$), 6.32 (1H, d, $J = 18.4$ Hz, Ar.CH:C*H*.B), 7.42 (1H, d, $J = 18.4$ Hz, Ar.C*H*:CH.B), 7.62 (2H, d, $J = 8.2$ Hz, ArHs), 7.85 (2H, d, $J = 8.2$ Hz, ArHs), 10.00 (1H, s, CHO). MS (FAB): 259 (100%, $M^+ + H$), 243 (17%, $M^+ - CH_3$). Accurate MS. Found: m/z 259.1552. $C_{15}H_{19}O_3B + H$ calc.: m/z, 259.1506. Anal. Found: C, 69.6; H, 7.3. $C_{15}H_{19}BO_3$ calc.: C, 69.8; H, 7.4%.

3.7. Preparation of p-nitrophenyl-1-vinylboronate (Table 1, number 26)

This nitro-substituted styrylboronate was prepared by the method described by *p*-methoxystyrylboronate but from 4-bromonitrobenzene (1.366 g, 6.67 mmol),

palladium(II) acetate (0.099 g, 0.40 mmol), triphenylphosphine (0.212 g, 0.81 mmol), tri-*n*-butylamine (3.22 ml, 13.53 mmol), vinylboronate **1** (1.250 g, 8.11 mmol) and dry toluene (10 ml). The mixture was refluxed for 67 h after which ^{1}H NMR analysis of the crude product indicated essentially quantative conversion to a 35-to-65 ratio of styrylboronate to styrene, and TLC showed that the products were inseparable in a wide range of different solvent systems. Purification by silica gel chromatography of the mixture (hexane, followed dichloromethane, as eluant) gave an orange oil (0.652 g) which was 45:55 mixture of styrylboronate:styrene but this was also heavily contaminated with triphenylphosphine oxide (as revealed by MS analysis of the product). Further purification was not possible without decomposition of the boronate. Evidence for the presence of the boronate came from ^{1}H NMR analysis of the mixture of products. ^{1}H NMR (300 MHz): δ (styrylboronate) 1.32 (12H, s, 4 × CH_3), 6.33 (1H, d, J = 18.4 Hz, CH.B), 7.41 (1H, d, J = 18.4 Hz, C*H*:CH.B), 7.60 (2H, d, J = 8.8 Hz, 2 × ArH) and 8.20 (2H, d, J = 8.8 Hz, 2 × ArH). δ (styrene) (^{1}H, 300 MHz) 5.50 (1H, d, J = 10.9 Hz, Ar.CH:CH*H*), 5.93 (1H, d, J = 17.6 Hz, Ar.CH:C*H*H), 6.78 (1H, dd, J = 10.9 and 17.6 Hz, Ar.C*H*:CHH), 7.42 (2H, d, J = 8.8 Hz, 2 × ArH) and 7.60 (2H, d, J = 8.8 Hz, 2 × ArH).

3.8. Preparation of naphthalene-1-vinylboronate (Table 1, number 29)

This compound was prepared by the method described for as *p*-methoxystyrylboronate but from 1-bromonaphthalene (0.50 ml, 3.61 mmol), palladium(II) acetate (0.060 g, 0.25 mmol), triphenylphosphine (0.131 g, 0.50 mmol), tri-n-butylamine (1.72 ml, 7.21 mmol), vinylboronate **1** (1.00 g, 6.49 mmol) and dry toluene (10 ml). The mixture was heated under reflux for 95 h. The crude oil obtained on work-up was subjected to by silica gel chromatography (hexane:diethyl ether, 95:5, then 90:10, as eluant) to give the Heck product as a colourless oil (0.490 g; 48%). IR (film): ν_{max} *inter alia* 1612 (C=C) cm^{-1}. ^{1}H NMR: (300 MHz): δ 1.36 (12H, s, 2 × C.Me_2), 6.27 (1H, d, J = 18.1 Hz, B.C*H*:CH), 7.44–7.56 and 7.73–7.87 (each 3H, m, ArHs), 8.22 (1H, d, J = 18.1 Hz, B.CH:C*H*), 8.27 (1H, d, J = 8.1 Hz, ArH). MS (FAB): m/z 280 (100%, M^+), 265 (30%, $M^+ - CH_3$), 181 (40%, $M^+ - C_6H_{11}O$). Accurate MS. Found: m/z 280.1632. $C_{18}H_{21}BO_2$ calc.: m/z 280.1635. Found: C, 76.9; H, 7.3. $C_{18}H_{21}BO_2$ calc.: C, 77.2; H, 7.6%.

3.9. Preparation of napthalene-1,8-divinylboronate (Table 1, number 30)

This compound was prepared by the method described for *p*-methoxystyrylboronate but from 1,8-diiodonaphthalene [9] (11.70 g, 30.10 mmol), palladium(II) acetate (0.113 g, 0.50 mmol), triphenylphosphine (1.31 g, 5.00 mmol), tri-*n*-butylamine (10.10 ml, 67.70 mmol), vinyl boronate **1** (10.43 g, 67.7 mmol) and dry toluene (50 ml). The mixture was refluxed for 72 h. After work-up the crude product was purified by silica gel chromatography (petroleum ether–ethyl acetate, gradient elution) gave an amorphous solid (11.35 g), which was dissolved in dichloromethane, decolourized with activated charcoal and precipitated by addition of *n*-hexane to give the Heck product **8** (9.99 g; 77%); m.p. 125–128°C. UV: λ_{max} (EtOH) 330 (ε = 14740), 262 (ε = 11900), 239 (ε = 37070), 208 (ε = 36420) nm. IR (KBr disc): ν_{max} *inter alia* 1620 (C=C) cm^{-1}. ^{1}H NMR (300 MHz): δ 1.32 (24H, s, 8 × CH_3), 6.08 (2H, d, J = 17.9 Hz, 2 × CH.B), 7.42 (2H, t, J = 7.7 Hz, 2 × ArH) 7.60 (2H, d, J = 7.1 Hz, 2 × ArH) and 7.77 (2H, d, J = 8.1 Hz, 2 × ArH), 8.06 (2H, d, J = 17.9 Hz, 2 × CH:CH.B). MS (FAB): 433 (17%, M^+ + H), and 83 (100%, C_6H_{11}). Anal. Found: C, 72.2; H, 8.1; B, 4.9. $C_{26}H_{34}B_2O_4$ calc.: C, 72.4; H, 7.9; B, 4.9%.

3.10. Preparation of 2-thiophenyl-1-vinylboronate (Table 1, number 33)

Silver(I) acetate (0.452 g, 2.71 mmol) and 2-iodothiophene (0.30 ml, 2.71 mmol) were added to a mixture of triphenylphosphine (0.028 g, 0.01 mmol), palladium(II) acetate (0.013 g, 0.05 mmol) and dry toluene (10 ml). Tri-*n*-butylamine (1.29 ml, 5.41 mmol) and vinylboronate 1 (0.750 g, 4.87 mmol) were then added; then the mixture was stirred at 110°C for 6 h diluted with diethyl ether (80 ml) and washed successively with 10% hydrochloric acid, water and saturated aqueous sodium chloride solution. The organic layer evaporated to give a brown oil which was purified by silica gel chromatography (hexane:diethyl ether, 97:3, as eluant) to give the Heck product as a yellow oil (0.296 g; 46%). IR (film) ν_{max} *inter alia* 1617 (C=C) cm^{-1}. ^{1}H NMR (300 MHz): δ 1.30 (12H, s, 2 × C.Me_2), 5.91 (1H, d, J = 18.1 Hz, B.C*H*:CH), 6.99 (1H, dd, J = 3.5 and 5.0 Hz, ArH), 7.08 (1H, d, J = 3.5 Hz, ArH), 7.24 (1H, d, J = 5.0 Hz, ArH), 7.47 (1H, d, J = 18.1 Hz, B.CH:C*H*). MS (FAB): m/z 236 (100%, M^+), 221 (23%, $M^+ - CH_3$), 136 (35%, $M^+ - C_6H_{12}O$). Accurate MS. Found: m/z 236.1035. $C_{12}H_{18}BO_2S$ calc.: m/z 236.1042.

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