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Hindered Organoboron Groups in Organic Chemistry. 30. The Production of *erythro*-1,2-Diols by the Condensation of Dimesitylboron Stabilised Carbanions with Aromatic Aldehydes[1,2]

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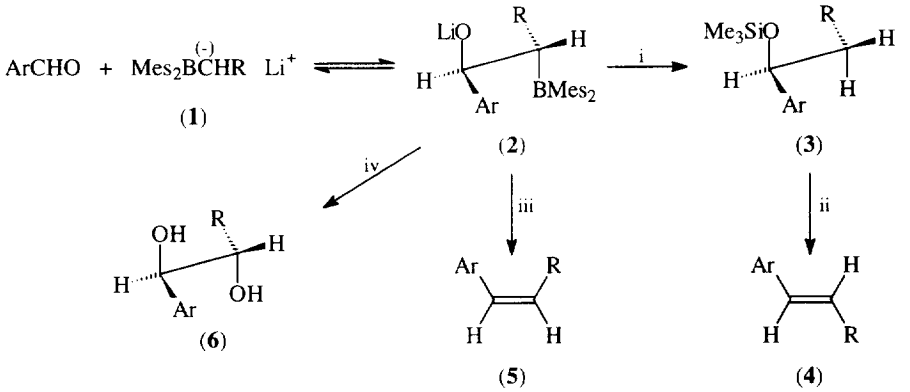
Abstract: . The condensation of dimesitylboron stabilised carbanions with a variety of aromatic aldehydes followed by *in situ* oxidation at low temperature, is a unique, highly stereoselective, direct and general process yielding predominantly *erythro*-1,2-diols.

We have previously[3] shown that the condensation of dimesitylboron stabilised carbanions (**1**) with aromatic aldehydes is a highly stereoselective process to give intermediates (**2**) that *via* (**3**) can give *E*-alkenes (**4**) or by treatment with trifluoroacetic anhydride can yield *Z*-alkenes (**5**) (Scheme 1).



i) TMSCl ; ii) HF/aq. CH_3CN ; iii) TFAA ; iv) $NaOH/H_2O_2$

Scheme 1

As part of the proof of structure of intermediate (**2a**) (Ar=Ph, R=Me)[3] it was oxidised at low temperature using alkaline hydrogen peroxide, a reaction that without exception proceeds with retention of configuration[4]. The major product was *erythro*-1-phenyl-1,2-dihydroxypropane (**6a**) (Ar=Ph, R=Me), and this together with the ^1H nmr spectrum of (**3a**) established the stereochemistry of the major isomer as (**2a**).

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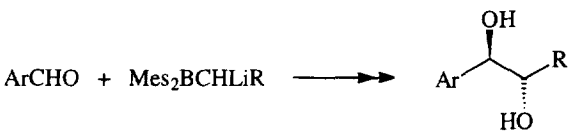
At this point it was realised that the one pot condensation of an aldehyde with a carbanion to yield eventually a 1,2-diol in a highly stereoselective fashion (equation 1) was a unique reaction in its own right and well worthy of further investigation.[2]



(1)

The reactions of (**1**) with aromatic aldehydes, as with the initial condensation of the Wittig reaction,[5] are reversible, in which case (**1**) can then react as bases to initiate Canizzaro reactions which destroy the aldehydes and lower the yields. The position of the equilibrium and the rate of the Canizzaro reaction varies with the substituents on both (**1**) and the aromatic aldehydes. Thus with (**1a**) it was impossible to directly obtain any alkene products and it was necessary to use both low temperatures and trapping techniques for successful reactions. Low temperatures are necessary to prevent equilibration and thus to allow intermediates (**2**) to be manipulated, and in the present case both the condensation and the oxidation must be carried out at as low a temperature as possible. In general the condensations were carried out at -116°C (though in many cases -78°C gave comparable yields) and aqueous alkaline at 0°C was added, followed by 30% hydrogen peroxide also at 0°C. The mixture was stirred at -116°C for 90 min. and then allowed to warm to 25°C.

We noted that intermediates (**2**) are themselves alkoxides, so that addition of further base should not be necessary. Some test oxidations of the reaction mixture derived from 4-nitrobenzaldehyde and $Mes_2BCHLiHept$ gave the results shown in Table 1.

Table 1 Production of *erythro*-$O_2NC_6H_4CHOHCHOHHept$

Experiment	Reagent	Yield (%)[a]
1	$NaOH/H_2O_2$	75
2	H_2O_2	74
3	Bu^tOOH/NEt_3	38
4	Bu^tOOH	25

a) hplc yields.

From experiments 1 and 2 it is clear that it is not necessary to add extra base for the oxidation and this broadens the scope of the reactions to include aldehydes bearing base sensitive groups. In order to carry out low temperature oxidations in anhydrous conditions we tried to use *t*-butyl hydroperoxide alone and in alkaline conditions.[6] However yields of diol were low and other products, probably derived from radical reactions were

evident. In practise we used alkaline hydrogen peroxide as our standard procedure and obtained the results shown in Table 2.

Table 2 Direct synthesis of ArCHOHCHOHR from ArCHO and $Mes_2BCHLiR$

Experiment	Product	Ar	R	Yield (%)[a]	*e* : *t*[b]	J(Hz) H-1, H-2	
						e	*t*
5	(**6a**)	C_6H_5	Me	84	95 : 5	3.9	7.5
6	(**6b**)	4-MeC_6H_4	Me	80	92 : 8	4.3	7.5
7	(**6c**)	4-ClC_6H_4	Me	86	90 : 10	4.0	7.4
8	(**6d**)	4-$O_2NC_6H_4$	Me	88	>99 : <1[c]	3.5	6.7[d]
9	(**6e**)	4-$MeOC_6H_4$	Me	84	>99 : <1[c]	4.2	-
10	(**6f**)	C_6H_5	Hept	80	93 : 7	4.7	6.9
11	(**6g**)	4-MeC_6H_4	Hept	74	95 : 5	4.5	7.1
12	(**6h**)	4-ClC_6H_4	Hept	62	90 : 10	3.9	7.0
13	(**6i**)	4-$O_2NC_6H_4$	Hept	53 (75)[e,f]	97 : 3	3.6	6.7
14	(**6j**)	4-$MeOC_6H_4$	Hept	57	98 : 2	4.4	7.2

a) Isolated yield of purified products. b) The ratio of *erythro* : *threo* products was obtained using ^1H nmr.

c) No *threo*-isomer was present in the experiment reported. d) From previous experiments.

e) Figure in parentheses is the h.p.l.c. yield. f) Lower yield due to isolation and purification difficulties.

In each case there was a strong predominance of one of the two diols. The diols *erythro*-(**6a**) and *threo*-(**6a**) are known and have rigorously proven structures.[7-9] The coupling constants are distinct and were used as a model for further structure assignment. In every experiment in Table 2 the predominent isomer is the one with the smallest coupling constant, and was assigned as the *erythro* isomer by analogy with (**6a**). In the case of (**6e**) the assignment was confirmed by an X-ray analysis. It should be noted that the chemical shift of H-1 for *erythro*-(**6a**) to (**6d**) was, on average 0.35 to lower field than for *threo*-(**6a**) to (**6d**) and for (**6f**) - (**6j**) was at 0.26 to lower field, the results being highly consistent.

A constant pattern between δ_c for *threo* and *erythro* C-1 and C-2 of the diol products was evident (Table 3). In every case the signal for the *threo* isomer was downfield of the signal for the *erythro*-isomer. The differences were somewhat more marked for the propan-1,2-diols (**6a**)-(**6e**) as compared with the nonan-1,2-diols (**6f**)-(**6j**) but were always in the same direction. The results appear to be diagnostic, although the lower

sensitivity of ^{13}C NMR compound with ^{1}H NMR makes it rather more difficult to analyse for very small proportions of a specific isomer.

Table 3 Differences in the ^{13}C nmr signals of *erythro*- and *threo*-1-aryl-1,2-diols

Diol	Signals* for C-1			Signals for C-2		
	erythro	*threo*	δ_{t-e}	*erythro*	*threo*	δ_{t-e}
(**6a**)	77.61	79.54	1.93	71.36	72.74	1.28
(**6b**)	77.42	79.36	1.94	71.30	72.22	0.92
(**6c**)	76.66	78.76	2.10	71.14	72.16	1.02
(**6d**)	76.3	-	-	71.02	-	-
(**6e**)	77.29	-	-	71.25	-	-
(**6f**)	77.03	77.89	0.86	75.21	75.98	0.77
(**6g**)	76.97	77.95	0.98	75.42	76.07	0.65
(**6h**)	76.30	77.19	0.89	75.08	75.93	0.85
(**6i**)	76.15	76.69	0.54	75.09	75.79	0.70
(**6j**)	76.7	-	-	75.1	-	-

* In ppm downfield from Me_4Si

The reaction was tested with success for $Mes_2BCHLiR$ with R=Me (experiments 5-9) and R=Hept (experiments 10-14) and we therefore assume that the results are reasonably general for all Mes_2BR^p. The aryl group was varied so that the aromatic aldehydes had *para*-positions substituted by H, Me, Cl, NO_2 and OMe groups. Despite the differing electronic nature of the substituents the yields and stereoselectivities were reasonably consistent, the highest selectivities being for 4-methoxy- and 4-nitrobenzaldehydes (experiments 8, 9, 13, 14). Despite the involvment of carbanions, 4-chlorobenzaldehyde gave yields comparable with the other aldehydes (experiments 7, 12). It was noticeable, however, that reactions with 4-chlorobenzaldehyde gave products with a somewhat lower diastereoselectivity (9:1) than obtained from other aldehydes. The rates of reaction varied somewhat, being very fast for 4-nitrobenzaldehyde and rather slow for 4-methoxybenzaldehyde. In general, isolated yields were somewhat lower for R=Hept compared with R=Me, though in part this reflects problems of purification.

It must be emphasised that the yields and diastereoselectivities of the reactions given in Table 3 depend on good temperature control. If the temperature is allowed to rise during the condensation and (or) the

oxidation steps, the yields are lowered and so are the diastereoselectivities of the products, due to stereochemical drift.[5]

We had hoped to check on the stereochemistry of the products by making cyclic phenylboronates and then checking on $J_{H\text{-}4,\ H\text{-}5}$. In the event this approach was not helpful. Due to the flexibility of the 1,3-dioxaborole ring the H-4, H-5 coupling constants for the major and minor boronates were not sufficiently different as to be diagnostic.

In summary, the low temperature condensation of aromatic aldehydes with dimesitylboron stabilised carbanions followed by *in situ* oxidation affords *erythro*-1,2-diols in a highly stereoselective fashion and in acceptable yields. The reaction is unique and has no parallel in the Wittig reaction,[5,10a] the Horner-Wadworth-Emmons reaction[10b] or the Peterson reaction.[10c,11]

EXPERIMENTAL

Instrumentation. Proton (^1H) and carbon (^{13}C) NMR spectra were obtained using a Bruker AC 400 NMR Spectrometer. Infra-red spectra were obtained using a Perkin Elmer 1725X FT-IR Spectrometer. UV spectra were obtained usign a Philips PU872 UV/VIS Scanning Spectrophotometer. HPLC anayses were performed using a 5μm Hypersil column (column size: 250mm x 4.9mm). The HPLC instrumentation included the Milton Roy constaMetric solvent delivery system, the Milton Roy C1 10B Integrator and LDC printer. Melting points were recorded on an Electrothermal digital melting point apparatus and are uncorrected. Mass spectra (low resolution EI/CI) were measured on a Fisons VG Quattrro II (UE Biotech) Spectrometer. Mass spectra (accurate mass EI) were taken on a VG ZAB-E Double Focussing Mass Spectrometer. Mass spectra (accurate mass CI with NH_3 (g)) was measured using the same mass spectrometer. Purification of the diols/phenylboronates was accomplished by spinning chromatography (Chromatotron) with a circular plate of 2mm silica gel (silica gel 60 PF_{254} Merck).

Reagents. All reactions involving organoboranes were performed using purified anhydrous reagents unless otherwise stated. Reagents were stored in desiccators over phosphorus pentoxide (P_2O_5) under an atmosphere of argon. Liquid aldehydes were dried and freshly distilled from calcium hydride (CaH_2) onto 4Å molecular sieves under argon, prior to use. Solid aldehydes were sublimed under reduced pressure , dried and stored as already outlined. Solutions of *tert*-butyllithium in hexanes (obtained from Aldrich Chemicals in 'Sureseal' bottles) were determined every two to three weeks by titration under inert atmosphere, against a standard solution of butan-2-ol using 2,2-dipyridyl as an indicator. Mesityl bromide was distilled under reduced pressure from calcium hydride onto molecular sieves (4Å).

Solvents: THF was purified firstly by passing through a column of activated alumina followed by distillation from calcium hydride under argon. Sodium (5g per litre) and benzophenone (4g per litre) were then

added to the THF in a still and the mixture was stirred under argon to give a purple solution of sodium benzophenone ketyl. The THF was then distilled from the ketyl under argon as required. Diethyl ether was passsed through activated alumina, dried by refluxing over calcium hydride then distilled as required.

Experimental Procedures: All glassware was oven dried (overnight at 190°C) assembled hot and allowed to cool under a stream of argon introduced *via* needles inserted through septum capped inlets, with outlets protected by oil bubblers. Syringes and double ended needles were dried overnight in the oven or flame dried and flushed with argon. The apparatus for reactions consisted of a dry three necked septum capped flask containing a magnetic follower. A bleed needle was inserted through the septum cap and a slight positive pressure of argon applied *via* an oil bubbler, thus allowing for any changes in pressure during the reaction.

1. General Procedure for the formation of 1,2-diols from dimesitylboron stabilised carbanion and aromatic aldehydes.

1.1. Production of the carbanions. Bromomesitylene (3.04 ml of 1M, 3.04 mmol) was placed in a dry round bottomed flask equipped with a magnetic follower. The flask was flushed with nitrogen, immersed in a cooling bath at -78°C and the solution well stirred. *tert*-Butyllithium (3.3 ml of 1.83 M, 6.1 mmol) was slowly added by syringe and the resultant reaction mixture was stirred at -78°C for 45 min. then warmed to 25°C over 25 min. during which time the solid that had precipitated dissolved up. The clear yellow solution of mesityllithium was added *via* nitrogen pressure on a double ended needle to a solution of alkyldimesitylborane (2.76 mmol) in THF (10 ml) at room temperature and the mixture was stirred for 2h. to give a red-orange solution of either $Mes_2BCHLiMe$ (from dimesitylethylborane[12]) or $Mes_2BCHLiHept$ (from dimesityloctylborane[12]).

1.2. Condensation of the carbanions with aromatic aldehydes. The carbanion solution prepared as above was cooled to -116°C in a liquid nitrogen - ethanol bath and stirred. The aromatic aldehyde (2.76 ml of a 1M solution in THF) was cooled to -116°C and then transferred to the well stirred carbanion solution *via* a cooled double ended needle. The mixture was stirred at -116°C for 2h.

1.3. Oxidation with alkaline hydrogen peroxide. Degassed sodium hydroxide solution (5.4 ml of 5M, 27 mmol) was cooled to 0°C and transferred by double ended needle to the stirred reaction mixture prepared as in 1.2. Hydrogen peroxide (9 ml of 30%, 90 mmol) solution at 0°C was then added in the same fashion and the mixture was stirred at -116°C for 90 min. before being allowed to slowly warm to 25°C. The reaction was stirred overnight.

1.4. Work-up followed by isolation of 1,2-diols. The reaction mixture was diluted with ether (50 ml), washed with saturated NaCl (2 x 20ml), dried ($MgSO_4$) and concentrated to afford crude product containing mesitylene and hydroxymesitylene. The crude product was purified by radial chromatography (Chromatotron) using a 2mm silica plate. Mesitylene and hydroxymesitylene eluted first with a 100:3 mixture of light petroleum/ethyl

acetate, followed by unreacted aldehyde and $ArCH_2OH$ using a 10:1 mixture of the same solvents. The diols are eluted with a 5:1 mixture.

1.5. Production of phenylboronates. A round bottomed flask was charged with diol (1.1 mmol) and phenylboronic acid (1.2 mmol) and then the mixture was dissolved in dry ether (5 ml). The flask was stoppered and allowed to stand overnight. Magnesium sulphate was added, the mixture filtered and the solvent removed. The product was purified by gradient elution with light petroleum/ethyl acetate from a 2mm silica plate on a Chromatotron.

2. Physical characteristics and yields of diols.

2.1. 1-Phenylpropan-1,2-diol, (**6a**) m.p. 79.8-82°C (84%) had ν_{max} 3300, 2900, 1350, 1000-1100 cm^{-1}, ν_{max} (EtOH) 260nm. δ_H 1.0 (3H, d, J=6.1Hz, H-3), 2.0 (1H, br. s., O*H*), 2.4 (1H, br. s., O*H*), 3.8 (0.05H, m, H-2, *threo*), 4.0 (0.95H, m, H-2, *erythro*), 4.3 (0.05H, d, J = 7.5Hz, H-1, *threo*), 4.6 (0.95H, d, J = 3.9Hz, H-1, *erythro*), 7.3 (5H, m, C_6H_5). (*erythro*:*threo* = 95:5), δ_C 17.2 (C-1), 71.3 (C-2, *erythro*), 77.5 (C-1, *erythro*), 126.6, 127.8, 128.4, 140.3 (aromatic carbons). (the *threo* isomer gave no visible peaks). m/z (CI), 170 (M + NH_4^+, 100); 152(M^+, 27), 108(15), 106(25), 52(27). Found, 170.1180; $(M + NH_4)^+$ requires 170.1181.

2.2 1-(4-Methylphenyl)propan-1,2-diol (**6b**) m.p. 72-75°C (80%) had ν_{max} 3400, 3200, 2900, 1500, 1050 cm^{-1}; λ_{max} 265nm. δ_H 1.1 (3H, d, J = 6.4Hz, H-3), 2.0 (1H, br. s., O*H*), 2.4 (3H, s, Ar-CH_3), 2.6 (1H, br. s. O*H*), 3.8 (0.08 H, m, H-2, *threo*), 4.0 (0.92H, m, H-2, *erythro*), 4.3 (0.08H, d, J = 7.5Hz, H-1, *threo*), 4.6 (0.92H, d, J = 4.3Hz, H-1, *erythro*), 7.1 (2H, d, J = 8.3Hz, aromatic protons), 7.2 (2H, d, J = 8.3Hz, aromatic protons). (*erythro*:*threo* = 92:8), δ_C 17.3 (C-3, *erythro*), 18.7 (C-3, *threo*), 21.13 (Ar-CH_3), 71.3 (C-2, *erythro*), 72.22 (C-2, *threo*), 77.42 (C-1, *erythro*), 79.36 (C-1, *threo*), 126.7, 129.0, 137.3, 137.5 (aromatic *C*, *erythro*). m/z (CI) 184 (M + NH_4^+, 42), 166(100), 149(25), 138(12), 122(10), 91(100). Found, $(M + NH_4)^+$. 184.1338; $C_{10}H_{18}NO_2$ requires 184.1338.

2.3 1-(4-Chlorophenyl)propan-1,2-diol (**6c**) (86%) was isolated as an oil ν_{max} 2900, 2700, 1450, 1370, 1100 cm^{-1}; λ_{max} 265 nm. δ_H 1.1 (3H, d, J = 7Hz, H-3), 2.2 (1H, br. s., O*H*), 2.8 (1H, br. s., O*H*), 3.8 (0.1H, m, H-2, *threo*), 4.0 (0.9H, m, H-2, *erythro*), 4.35 (0.1H, d, J = 7.4Hz, H-2, *threo*), 4.65 (0.9H, d, J = 4.0Hz, *erythro*), 7.2-7.3 (4H, m, Ar-H); δ_C, 17.0 (C-3), 71.14 (C-2, *erythro*), 72.16 (C-2, *threo*), 76.66 (C-1, *erythro*), 78.76 (C-1, *threo*), 128, 128.2, 133.5, 138.7 (*erythro*). m/z (CI), 206 (M + NH_4^+, 30), 204 $(M + NH_4)^+$ (100), 191(40), 186(50), 166(25), 152(20), 135(57), 94(18). Found, $(M + NH_4)^+$ 204.0791. $C_9H_{15}NO_2Cl$ requires 204.0791.

2.4. 1-(4-Nitrophenyl)propan-1,2-diol (**6d**) (88%) was isolated as orange needles m.p. 76-83°C, ν_{max} 3300, 2900, 1500, 1350, 1100 cm^{-1}, λ_{max} 274nm. δ_H 1.0 (3H, d, J = 6.4Hz, H -3), 2.3 (1H, br. s., O*H*), 3.0 (1H, br.

s., O*H*), 3.8 (0.03H, m, H-2, *threo*), 4.1 (0.97H, m, H-2, *erythro*), 4.5 (0.03H, d, J = 6.7Hz, H-1, *threo*), 4.9 (0.93H, d, J = 3.53Hz, H-1, *erythro*), 7.5 (2H, d, J = 8.9Hz aromatic), 8.2 (2H, d, J = 8.9Hz, aromatic). δ_C, 16.8 (C-3, *erythro*), 71.0 (C-2, *erythro*), 76.3 (C-1, *erythro*), 123.5, 127.4, 147.4, 147.7 (aromatic C, *erythro*). m/z (c.i.) 167(10), 150(40), 139(16), 122(100). Found, $(M + NH_4)^+$ (CI) 215.1032. $C_9H_{15}O_4N_2$ requires 215.1032.

2.5 1-(4-Methoxyphenyl)propan-1,2-diol. (**6e**) (84%) was isolated as crystals m.p. 107-109°C, ν_{max} 3300, 2900, 1500, 1250, 1050 cm^{-1}, λ_{max} 276 nm. δ_H 1.1 (3H, d, J = 6.26Hz, H-3), 1.9 (1H, br. s. O*H*), 2.4 (1H, br. s. O*H*), 3.8 (3H, s, OCH_3), 4.0 (1H, m, H-2, *erythro*), 4.6 (1H, d, J = 4.2 Hz, H-1, *erythro*), 6.9 (2H, d, J = 8.2 Hz, Ar-H), 7.3 (2H, d, J = 8.6Hz, Ar-H), δ_C (*erythro*) 17.6 (C-3), 55.3 (OCH_3), 71.2 (C-2), 77.3 (C-1), 113.8, 127.9, 132, 159 (aromatic C). m/z (C.I.), 200(7), 182(50), 165(100), 151(15), 137(15). Found $(M + NH_4)^+$, 200.1287. $C_{10}H_{18}NO_3$ requires 200.1287.

2.6 1-Phenylnonan-1,2-diol. (**6f**) (67%) was isolated as a colourless oil. ν_{max} 3300, 2900, 1677, 1639, 1500 cm^{-1}, λ_{max} 256 nm. δ_H 0.8 (3H, q, C-9), 1.1-1.4 (12H, m, H-3 to H-8), 1.8-2.4 (2H, br. 2 x O*H*), 3.75 (0.1H, m, H-2, *threo*), 3.8 (0.9H, m, H-2, *erythro*), 4.4 (0.1H, d, J = 6.9Hz, H-1, *threo*), 4.7 (0.9 H, d, J = 4.36Hz, H-1, *erythro*), 7.33-7.56 (5H, m, C_6H_5). δ_C 75.21 (C-2, *erythro*), 75.98 (C-2, *threo*), 77.03 (C-1, *erythro*), 77.89 (C-1, *threo*) 14.08 (C-9). m/z (CI, NH_3), 254(M + NH_4^+, 10), 236 (M, 20), 135 (62). Found, $(M + NH_4)^+$. 254.2220, $C_{15}H_{28}NO_2$ requires 254.2253.

2.7 1-(4'-Methylphenyl)nonan-1,2-diol. (**6g**) (74%) was isolated as an oil. ν_{max}, 3385, 2826, 1490cm^{-1}, λ_{max} 265 nm. δ_H 0.98 (3H, t, J = 6.4Hz, C-9), 1.2-1.5 (12H, m, H-3 to H-8), 2.35 (3H, s, Ar-CH_3), 3.76 (0.05H, m, H-2, *threo*), 3.8 (0.95H, m, H-2, *erythro*), 4.4 (0.05H, d, J = 7.06Hz, H-1, *threo*), 4.61 (0.95H, d, J = 4.52Hz, H-1, *erythro*), 7.17 (2H, *d*, J = 8Hz, Ar-*H*), 7.24 (2H, *d*, J = 8Hz, ArH). δ_C 14.17 (C-9), 22.73 (C-8), 25.83 (C-7), 29.28, 29.39 (C-6, C-5), 31.42, 31.94 (C-4, C-3), 75.42 (C-2, *erythro*), 76.07 (C-2, *threo*), 76.97 (C-1, *erythro*), 77.95 (C-1, *threo*). m/z (c.i.) 268(M + NH_4^+, 8), 250(20, M^+), 233(47), 122(100, ArCHO). Found, $(M + NH_4)^+$. 268.2277. $C_{16}H_{30}NO_2$ requires 268.2277.

2.8 1-(4'-Chlorophenyl)nonan-1,2-diol. (**6h**) (62%) was isolated as a thick oil. ν_{max} 3320, 2827. 2856. 1598 cm^{-1}. λ_{max} 265 nm. δ_H 0.86 (3H, t, J = 7.0Hz, H-9), 1.1-1.35 (10H, m, H-8 to H-4), 1.45 (2H, m, H-3), 3.10 (1H, br. s., O*H*), 2.3 (1H, br. s., O*H*), 3.76 (1H, m, H-2, *erythro*), 4.4 (0.1H, d, J = 6.97Hz, H-1, *threo*), 4.62 (0.9H, d, J = 3.88Hz, H-1, *erythro*). 7.27 (2H, d, J = 8.1Hz, H-2'), 7.30 (2H, d, J = 8Hz). δ_C (*erythro*), 14.09 (C-9), 22.61 (C-8), 25.70 (C-7), 29.18, 29.22 (C-6, C-5), 31.77, 32.64 (C-4, C-3), 75.08 (C-2), 76.30 (C-1), 128.19, 128.40 (C-2', C-3'), 133.44 (C-1'), 138.84 (C-4'), δ_C (*threo*), 75.93 (C-2), 77.19 (C-1), 133.69 (C-1'), 139.75 (C-4'). m/z 290, 288($M^{+\cdot}$, 30, 10), 259, 257(35, 60), 240(24), 221(35), 179(20), 152(30), 135 (60). Found, 288.1730. $C_{15}H_{27}NO_2{}^{35}Cl$ requires 288.1730.

2.9 1-(4′-Nitrophenyl)nonan-1,2-diol. (**6i**) (53%) was isolated as a yellow oil. ν_{max}, 3300, 2900, 1700, 1600, 1450, 1350, 1050 cm^{-1}. λ_{max} 275 nm. δ_H 0.84 (3H, t, 7.0Hz, H-9), 1.15-1.30 (10H, m, H-8 to H-4), 1.42 (2H, m, H-3), 3.05 (2H, br. s. O*H*), 3.6 (0.03H, m, H-2, *threo*), 3.8 (0.97H, m, H-2, *erythro*), 4.5 (0.03H, d, J = 6.7Hz, H-1, *threo*), 4.8 (1H, d, J = 3.6Hz, H-1, *erythro*), 7.49 (2H, d, J = 9Hz, H-3′), 8.13 (2H, d, J = 9Hz, H-2′). δ_C 14.07 (C-9), 22.61 (C-8), 25.90 (C-7), 29.21, 29.29 (C-6, C-5), 31.01 (C-4), 31.77 (C-3), 75.09 (C-2, *erythro*), 75.79 (C-2, *threo*), 76.15 (C-1, *erythro*), 76.69 (C-1, *threo*), 123.28 (C-2′), 127.65 (C-3′), 147.17 (C-1′), 148.21 (C-4′). m/z (CI) 299($M + NH_4^+$, 57), 251(100), 234(40), 139(60), 135(34), 122(48), 52(60). Found ($M + NH_4^+$) 299.1971. $C_{15}H_{27}N_2O_4$ requires 299.19708.

2.10 1-(4′-Methoxyphenyl)nonan-1,2-diol. (**6j**) (57%) was isolated as a pale yellow oil. ν_{max} , 3312, 3040, 2955, 2917, 1635, 1615 cm^{-1}, λ_{max} 275nm. δ_H 0.86 (3H, t, J = 7.0Hz, H-9), 1.2-1.26 (10H, m, H-4 to H-8), 1.86 (1H, d, 0.6Hz, O*H*), 2.48 (1H, d, J = 3Hz, O*H*), 3.80 (1H, m, H-2, *erythro*), 3.80 (3H, s, OCH_3), 4.35 (0.02H, d, J = 7.14 Hz, H-1, *threo*), 4.60 (0.98H, d, J = 4.43Hz, H-1, *erythro*), 6.88 (2H, d, J = 9 Hz, H-2′), 7.24 (2H, d, J = 9 Hz, H-3′). δ_C 14.1 (C-9), 22.6 (C-8), 25.9 (C-7), 29.2, 29.6 (C-6, C-5), 31.8, 31.9 (C-4, C-3), 55.2 (OCH_3), 75.1 (C-2, *erythro*), 76.7 (C-1, *erythro*), 113.7 (C-3′), 128.1 (C-2′), 132.5 (C-1′), 147.2 (C-4′). m/z (CI) 266(M^+, 15), 249(48), 138(28), 137(100), 121(28). Found, 266.1882. $C_{16}H_{26}O_3$ requires 266.18819.

3. Physical characteristics and yields of phenylboronates prepared from some 1,2-diols described in Section 2.

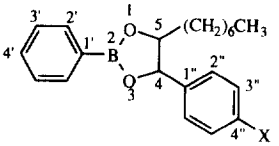
3.1 Using the general procedure described in Section 1.5, *5-heptyl-4-(4"-methylphenyl)-2-phenyl-1,3-dioxa-2-boracyclopentane** was isolated as a colourless oil in 85% yield. δ_H, 0.85 (3H, t, J=7Hz, CH_2 CH_3), 1.0-1.5 (12H, m, $(CH_2)_6$), 2.3 (3H, s, Ar-CH_3), 4.3 (0.04H, ddd, J=4,8,9Hz, H-5, *threo*), 4.7 (0.96 H, ddd, J=4,8,9Hz, H-5, *erythro*), 5.0 (0.04 H, d, J=7Hz, H-4, *threo*), 5.8 (0.96 H, d, J=8Hz, H-4, *erythro*), 7.1 (4H, s, H-2", 3"), 7.4 (2H, ddd, J=2,8,11Hz, H-3'), 7.5 (1H, dd, J=2, 11 Hz, H-4'), 7.9 (2H, dd, J=1,8Hz, H-2'). *erythro* : *threo* = 96.4 : 3.6. δ_C† 14.0 (CH_2 CH_3), 21.0 (Ar-CH_3), 22.6, 26.1, 29.2, 29.4, 31.7, 32.7 (($CH_2)_6$), 81.3 (C-5), 81.8 (C-4), 126.5, 126.8, 127.9, 129.1, 131.6, 135.0, 135.1, 137.6, (aromatic carbons). m/z (e.i.) 336(M^+, 34), 321(26), 237(38), 193(27), 147(35), 119(33), 105(100), 104(67), 103(53), 91(48). δ_B 31.37. Found, M^+ = 336.2261, $C_{22}H_{29}BO_2$ requires 336.2261.

3.2 5-Heptyl-4-(4"-methoxyphenyl)-2-phenyl-1,3-dioxa-2-boracyclopentane was isolated as a colourless oil in 86% yield. δ_H 0.9 (3H, t, J=7Hz, CH_2 CH_3), 1.1-1.5 (12H, m, $(CH_2)_6$), 3.8 (3H, s, OCH_3), 4.3 (0.04H, ddd, H-5, *threo*), 4.7 (0.96H, ddd, J=4,8,10Hz, H-5, *erythro*), 5.0 (0.04H, d, J=6Hz, H-4, *threo*), 5.6 (0.96H, d, J=8Hz, H-4, *erythro*), 6.9 (2H, dd, J=8.4, H-3"), 7.2 (2H, d, J=8.4Hz, H-2"), 7.4 (2H, dd, J=1,8Hz, H-3'), 7.5

(1H, m, H-4'), 7.9 (2H, dd, J=1,8Hz, H-2'). *erythro* : *threo* = 96 : 4. δ_C†, 14.1 (CH_2 CH_3), 22.6, 26.1, 29.2, 29.5, 31.7, 32.9 (CH_2)$_6$), 55.2 (OCH_3), 81.3 (C-5), 81.6 (C-4), 113.6 (C-1'), 127.6, 130.1q, 131.6, 135.1 (aromatic carbons), 159.0q (C-4"). δ_B 31.33 m/z (e.i.) 352(M^+, 42), 321(18), 253(24), 209(39), 163(22), 135(47), 121(100), 120(48), 105(73), 91(45). Found, M^+ = 352.2210. $C_{22}H_{29}BO_3$ requires 352.29097.

3.3 5-Heptyl-4-(4"-nitrophenyl)-2-phenyl-1,3-dioxa-2-boracyclopentane was isolated as a yellow oil in 92% yield. δ_H 0.8 (3H, t, J=7Hz, CH_2 CH_3), 0.9-1.4 (12H, m, (CH_2)$_6$), 4.2 (0.02H, m, H-5, *threo*), 4.7 (0.98H, ddd, J=4,8,10Hz, H-5, *erythro*), 5.1 (0.02H, d, J=6Hz, H-4, *threo*), 5.7 (0.98H, d, J=8Hz, H-4, *erythro*), 7.3-7.4 (4H, m), 7.44 (1H, dd, J=1.6, 8.0Hz, H-4'), 7.84 (2H, dd, J=1.2, 8.0Hz, H-2'), 8.14 (2H, d, J=8.0Hz, H-3"). δ_C, 14.1 (CH_2-CH_3), 22.6, 25.8, 29.3, 29.4, 31.7, 33.1 ((CH_2)$_6$), 80.8, 80.9 (C-4, 5), 123.5, 127.6, 127.9, 128.0, 128.4, 132.0, 133.7, 135.1, 145.7q, 147.6q (aromatic carbons) m/z (e.i.), 367 (M^+, 12), 268(42), 193(34), 136(23), 107(51), 105(100), 89(90). Found, M^+ = 367.1955. $C_{21}H_{26}NO_4B$ requires 367.1955.

* The numbering used is as shown



†All figures for *erythro* isomer

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