Reaction of Arylboronic Acids and their Derivatives with Lead Tetra-acetate. The Generation of Aryl–lead Triacetates, and *meta*- and *para*-Phenylenebis(lead triacetate), *in situ* for Electrophilic Arylation

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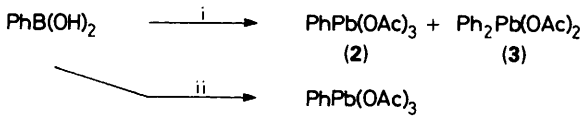
Arylboronic acids and some of their derivatives have been found to undergo a rapid boron–lead exchange with lead tetra-acetate. In the presence of a catalytic amount of mercury(II) acetate, the reaction produces mainly the aryl–lead triacetate, and it has been developed as a convenient method for *in situ* generation of these useful electrophilic C-arylating reagents. The reaction allows the generation for the first time of *meta*- and *para*-phenylenebis(lead triacetate), compounds which behave as *meta*- and *para*-phenylene dication equivalents.

The utility of aryl–lead triacetates as electrophilic arylating agents is now well established,[1,2] The synthesis of these compounds may be achieved by direct plumbation,[3] mercury–lead exchange,[2,3] tin–lead exchange,[4] and in certain cases by silicon–lead exchange.[3] Because of the nature of these reactions and/or other products of the reactions, only the reaction of a diarylmercury with lead tetra-acetate[2] has lent itself to the *in situ* generation of the aryl–lead reagent and subsequent arylation of a carbon nucleophile. We now report a simpler method which is more economical in terms of aryl group transfer than the mercury–lead exchange route, in which only one of the aryl groups of the diarylmercury compound is transferred to lead (Reaction 1).

The well known boron–mercury exchange of arylboronic acids[5] prompted us to examine the reaction of these compounds with lead tetra-acetate as a possible route to aryl–lead triacetates. When phenylboronic acid (**1a**) was added slowly to a deuteriochloroform solution of lead tetra-acetate at 40 °C there was a rapid reaction, and analysis of the crude reaction mixture by ^{1}H NMR spectroscopy showed that the major product (*ca.* 80%) was phenyl–lead triacetate (**2**); however, a significant amount (*ca.* 20%) of diphenyl–lead diacetate (**3**) was also produced. By carrying out the reaction under similar conditions in the presence of a catalytic amount (10%) of mercury(II) acetate, the formation of the diphenyl–lead compound (**3**) was suppressed, and the NMR spectrum of the reaction mixture indicated that phenyl–lead triacetate was produced in high yield † (see Scheme 1).

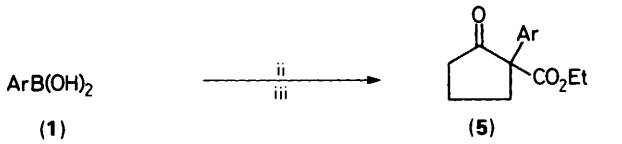
$$Ar_2Hg + Pb(OAc)_4 \longrightarrow ArPb(OAc)_3 + ArHgOAc \quad (1)$$



Scheme 1. *Reagents and conditions:* i, $Pb(OAc)_4$, $CHCl_3$, 40 °C; ii, $Pb(OAc)_4$, 10% $Hg(OAc)_2$, $CHCl_3$, 40 °C.

Although the above method gives high yields of aryl–lead triacetates in solution, and may be used to obtain the pure compounds (see later), the isolation procedure in the tin–lead exchange reaction[4] (Reaction 2) is simpler and it remains our preferred route to these reagents. The mercury-catalysed boron–lead exchange reaction outlined in Scheme 1, however, appeared to offer a convenient means of generating an aryl–lead triacetate in solution for subsequent reaction with a nucleophile. To investigate this possibility, chloroform solutions of a number of aryl–lead triacetates were generated from the corresponding arylboronic acids, and treated with ethyl 2-oxocyclopentanecarboxylate (**4**) in the presence of pyridine as indicated in Scheme 2. For all six arylboronic acids (**1a–f**), investigated, substitution of the β-keto ester (**4**) occurred, to give the α-arylated β-keto esters (**5a–f**) in moderate to good yields (see entries 1–6, Table). The method is clearly superior to the mercury–lead exchange route[2] referred to above, where only one of the two aryl groups of the diarylmercury compound is used, while it is also more efficient than employing isolated aryl–lead triacetates[6] because of losses which occur in their purification.

$$ArSnBu_3 + Pb(OAc)_4 \xrightarrow{i} ArPb(OAc)_3 + Bu_3SnOAc \quad (2)$$



(1) (5)

a; Ar = Ph
b; Ar = *p*-$CF_3C_6H_4$
c; Ar = *p*-$MeOC_6H_4$
d; Ar = *o*-$MeOC_6H_4$
e; Ar = 2,4,6-$Me_3C_6H_2$
f; Ar = *m*-$NO_2C_6H_4$

Scheme 2. *Reagents and conditions:* i, $Hg(OCOR)_2$ (cat.), $CHCl_3$, 40–60 °C; ii, $Pb(OAc)_4$, $Hg(OCOR)_2CHCl_3$; iii, ethyl 2-oxocyclopentane-2-carboxylate (**4**), pyridine.

It can be seen from the Table that the presence of an electron-withdrawing group in the benzene ring results in lower yields (entries 2 and 6), and we attribute this to a slower boron–lead exchange reaction in these cases. For example, with *m*-nitrophenylboronic acid (**1f**), it was necessary to carry out the reaction with lead tetra-acetate at 60 °C and with 20% mercury(II) trifluoroacetate as catalyst instead of our generally used conditions [10% mercury(II) acetate and 40 °C]. The low yield of the mesityl derivative (**5e**) (entry 5) is believed to be due

† If the order of addition is reversed, *i.e.* lead tetra-acetate is added to a mixture of phenylboronic acid and mercury(II) acetate, a significant amount of the diphenyllead compound (**3**) is produced.

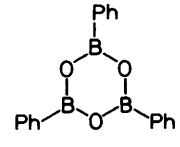
Table. Reactions of the β-keto ester (**4**) with aryl–lead triacetates generated *in situ* from arylboronic acids and their derivatives.

Entry	Arylboron compd.	Method[a]	Product	Isolated yield (%)
1	(**1a**)	A	(**5a**)	77
2	(**1b**)	A	(**5b**)	58
3	(**1c**)	A	(**5c**)	74
4	(**1d**)	A	(**5d**)	78
5	(**1e**)	A	(**5e**)	26
6	(**1f**)	B	(**5f**)	40
7	(**6**)	A	(**5a**)	76
8	(**7**)	A	(**5a**)	75

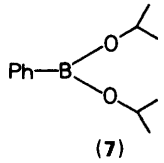
[a] For the methods see Experimental section.

to steric inhibition in the arylation step and/or proto-demetallation of the intermediate mesityl–lead compound. The isolation of a significant amount of mesitylene would suggest that the latter reaction is occurring.

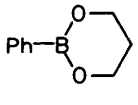
In the light of the above result obtained with mesitylboronic acid (**1e**), we briefly examined some derivatives of boronic acids to reduce the possibility of proto-demetallation. Triphenylboroxin (**6**), which is simply obtained by heating phenylboronic acid, was the first derivative examined. Unlike the parent acid (**1a**), it was very slow to react with lead tetra-acetate in the absence of mercury(II) catalyst, and even after 20 h the reaction was incomplete; both phenyl–lead triacetate (**2**) and diphenyl–lead diacetate (**3**) were present (^{1}H NMR spectroscopy), with compound (**3**) being the major product. However, when the boroxin (**6**) was added to a chloroform solution of lead tetra-acetate containing 10% mercury(II) acetate, there was rapid formation of phenyl–lead triacetate (**2**) (complete within 45 min) and the diphenyl–lead compound (**3**) could not be detected. Reaction of such a mixture with β-keto ester (**4**) in the presence of pyridine led to the formation of the arylated keto ester (**5a**) in similar yield to that obtained with phenylboronic acid (**1a**) (entry 7, Table).



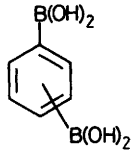
(**6**)



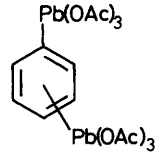
(**7**)



(**8**)

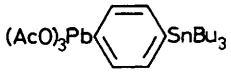


(**9**) *para*
(**10**) *meta*



(**11**) *para*
(**12**) *meta*

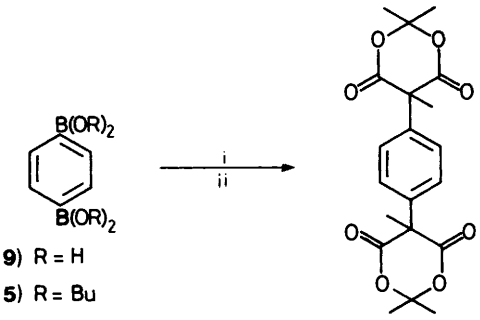
(**13**)



(**14**)

Two esters of phenylboronic acid, compounds (**7**) and (**8**), were also examined in the arylation sequence of Scheme 2, but no improvement in the yield of the keto ester (**5a**) could be achieved. Di-isopropyl phenylboronate (**7**) underwent a rapid mercury(II)-catalysed exchange reaction with lead tetra-acetate (complete within 10 min) to give only the lead compound (**2**). Addition to the keto ester (**4**) to this solution under the usual conditions gave the arylated compound (**5a**) in a similar yield to that obtained above (see entry 8, Table). In sharp contrast to the behaviour of the di-isopropyl ester (**7**), the cyclic ester (**8**) showed very little reaction with lead tetra-acetate under the same conditions after 20 min. After 2 days the reaction was still not complete, although from the ^{1}H NMR spectrum it appeared that, like the other mercury(II)-catalysed reactions, only phenyl–lead triacetate (**2**) was being produced.

The ease with which arylboronic acids reacted with lead tetra-acetate prompted us to examine the possibility of converting the phenylenediboronic acids (**9**) and (**10**) into the corresponding bis(triacetoxyplumbyl) derivatives (**11**) and (**12**), compounds which might be expected to behave as *para*- and *meta*-phenylene dication equivalents. An earlier attempt to produce the dilead compound (**11**) from the distannyl derivative (**13**) by the relatively slow tin–lead exchange reaction had proved to be unsuccessful; the reaction with 2 equiv. of lead tetra-acetate gave rise to *p*-(tributylstannyl)phenyl–lead triacetate (**14**), which did not undergo further reaction. On the other hand, *p*-phenylenediboronic acid (**9**) reacted readily with 2 equiv. of lead tetra-acetate and a catalytic amount of mercury(II) acetate to give the dilead compound (**11**). Although compound (**11**) could not be purified for elemental analysis, it had the expected spectral properties, and, on addition of methyl Meldrum's acid (**16**) to the above reaction mixture, the *para*-disubstituted compound (**17**) was produced in 45% yield (see Scheme 3).* The



(**9**) R = H
(**15**) R = Bu

(**17**)

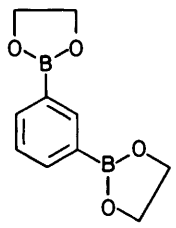
Scheme 3. *Reagents and conditions:* i, $Pb(OAc)_4$ (2 equiv.), $Hg(OAc)_2$, $CHCl_3$; ii, 2,2,5-trimethyl-1,3-dioxane-4,6-dione (**16**) (3 equiv.), pyridine, 60 °C.

tetrabutyl diester (**15**) underwent a more rapid exchange with lead tetra-acetate than the parent acid (**9**), and when the reaction mixture was treated in the same way with the Meldrum's acid derivative (**16**), as outlined in Scheme 3, a similar yield (49%) of the product (**17**) was obtained.

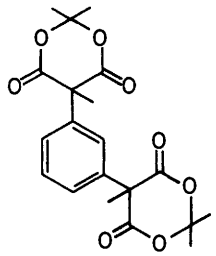
Attempts to produce the *m*-phenylenedilead compound (**12**) by reaction of the corresponding diboronic acid (**10**) with lead tetra-acetate failed due to the insolubility of the acid (**10**) in chloroform. However, it was readily converted into the diester (**18**), which was soluble and underwent mercury-catalysed boron–lead exchange to give the dilead compound (**12**). Although, as with the *para*-isomer (**11**), purification of the isolated compound could not be achieved, solutions of compound (**12**), generated as above, may be used as a *m*-phenylene dication equivalent, as demonstrated in the formation of the *meta*-disubstituted benzene derivative (**19**) in 44% yield when treated with the Meldrum's acid derivative (**16**).

As mentioned above, the reaction of arylboronic acids with

* The β-dicarbonyl compound (**16**) was used instead of our usual model substrate (**4**) to avoid the formation of a mixture of diastereoisomers.



(18)



(19)

$ArPb(OAc)_3$

(20) Ar = p-$CF_3C_6H_4$

(21) Ar = p-$MeOC_6H_4$

(22) Ar = o-$MeOC_6H_4$

(23) Ar = 2,4,6-$Me_3C_6H_2$

lead tetra-acetate was explored as a method for the preparation of a number of aryl–lead triacetates, but was found to be less convenient than our tin–lead exchange route.[4] This results from the necessity to wash the chloroform solution of the lead compound with water, a process that may cause formation of polymer,[3] which requires treatment with acetic acid to regenerate the monomer. Nevertheless, the method does provide a useful alternative to the route *via* aryltributylstannanes, and its scope has been briefly explored in syntheses of the aryl–lead triacetates (**2**) and (**20**)–(**23**), which were obtained in yields of 33–74%.

Synthesis of the Boronic Acid (**1b**) *and Bis-stannane* (**13**).—*p*-Trifluoromethylphenylboronic acid (**1b**), which had not been previously prepared, was readily obtained from 4-bromo-α,α,α-trifluorotoluene, by treatment of the derived lithium compound with triethyl borate at low temperature; however, due to the ease of dehydration of the acid (**1b**), even at room temperature, it could not be obtained free of the trimer, tris(*p*-trifluoromethylphenyl)boroxin, and thus its characterisation was completed by dehydration to the boroxin at 200 °C.

p-Phenylenebis(tributylstannane) (**13**) had been reported previously,[7] but the data recorded in that work would suggest that the material obtained was recovered tributyltin chloride. The preparation of compound (**13**) was readily achieved, albeit in modest yield, from the di-Grignard intermediate, which was formed from *p*-dibromobenzene.

Experimental

M.p.s are uncorrected. IR spectra were recorded on a Digilab FTS-80 spectrometer, and UV spectra were obtained on a Perkin-Elmer 402 apparatus. NMR spectra were determined with $SiMe_4$ as internal standard on Varian EM-390, Varian XL-100 and Bruker MW-400 spectrometers. Mass spectra were obtained with an AE1 MS-902 instrument. Column chromatography was carried out with Merck Kieselgel 60 (230–400 mesh). Light petroleum refers to the fraction of b.p. 60–80 °C. Analyses were performed by the Australian Microanalytical Service, Melbourne. Lead tetra-acetate (Merck) was kept at 1 mmHg over KOH pellets to remove excess of acetic acid. Phenylboronic acid was purchased from Aldrich Chemical Company.

Reactions of the β-Keto Ester (**4**) *with Aryl–lead Triacetates generated* in situ *from Arylboronic Acids and Their Derivatives as Reported in the Table.—Method A.* The arylboron compound (5.0 mmol) was added over 15 min to a stirred mixture of lead tetra-acetate (5.0 mmol) and mercury(II) acetate (0.5 mmol) in chloroform (7.6 ml) at 40 °C. The mixture was stirred at 40 °C for 1 h and then overnight at room temperature.* Ethyl 2-oxocyclopentanecarboxylate (**4**) (0.710 g, 4.55 mmol) in pyridine (1.197 g, 15.15 mmol) was then added, and the mixture was stirred at 40 °C for 1 h, and then at room temperature overnight.

The reaction mixture was filtered at the pump through Celite, and the solid was washed with chloroform (3 × 15 ml). The filtrate was shaken with sulphuric acid (3M; 25 ml), and the chloroform layer was separated. The aqueous phase was extracted with chloroform (2 × 15 ml), and the combined chloroform extracts were dried (Na_2SO_4), filtered, and evaporated. The brown residue was dissolved in ether (100 ml) and the solution cooled to 0 °C and shaken briefly with ice-cold aqueous sodium hydroxide (3M; 50 ml) and then with water (50 ml), and finally brine (50 ml). The ether solution was then dried (Na_2SO_4) and evaporated. The crude product was purified as indicated below.

Method B. As for method A except that mercury(II) trifluoroacetate (1.0 mmol) was used, and the boron–lead exchange reaction and the keto ester arylation step were each conducted at 60 °C for 1 h and then kept at room temperature overnight.

The following compounds were synthesised by the above methods. (i) Ethyl 2-oxo-1-phenylcyclopentanecarboxylate (**5a**), prepared by method A from phenylboronic acid, was obtained as an oil (0.8 g, 77%), identical (IR and NMR spectra) with an authentic sample.[2]

(ii) *Ethyl 2-oxo-1-(p-trifluoromethylphenyl)cyclopentanecarboxylate* (**5b**) was obtained by method A and column chromatography in light petroleum–ether (9:1) as an oil (0.79 g, 58%) (Found: C, 60.0; H, 4.9; F, 19.0. $C_{15}H_{15}F_3O_3$ requires C, 60.0; H, 5.0; F, 19.0); λ_{max}(EtOH) 237, 259sh, 265, and 271 nm (ε 1 200, 550, 630, and 530); ν_{max}($CHCl_3$) 1 755, 1 725, and 1 620 cm^{-1}; δ_H($CDCl_3$) 1.22 (3 H, t, J 7.0 Hz, CH_3), 1.80–3.08 (6 H, m, 3 × CH_2), 4.19 (2 H, q, J 7.0 Hz, OCH_2), and 7.59 (4 H, s, ArH); m/z 300 (M^+), 281 (M^+ − F), 272 (M^+ − CO), 243, and 227 (M^+ − CO_2Et).

(iii) Ethyl 1-(*p*-methoxyphenyl)-2-oxocyclopentanecarboxylate (**5c**) was obtained by method A as an oil (0.88 g, 74%), which was identical (IR and NMR spectra) with an authentic sample.[6]

(iv) Ethyl 1-(*o*-methoxyphenyl)-2-oxocyclopentanecarboxylate (**5d**) was obtained by Method A as an oil (0.93 g, 78%), which was identical (IR and NMR spectra) with an authentic sample.[2]

(v) *Ethyl 1-mesityl-2-oxocyclopentanecarboxylate* (**5e**) was obtained by method A and column chromatography in light petroleum–ether (24:1) as an oil (0.32 g, 26%) (Found: C, 74.5; H, 8.5. $C_{17}H_{22}O_3$ requires C, 74.4; H, 8.1%); ν_{max}(film) 1 760, 1 720, 1 715, and 1 620 cm^{-1}; δ_H($CDCl_3$) 1.01 (3 H, t), 2.12 (6 H, s, 2 × CH_3), 2.22 (3 H, s, CH_3), 1.80–3.36 (6 H, m, 3 × CH_2), 4.0–4.4 (2 H, m, OCH_2), and 6.81 (2 H, s, ArH); m/z 274 (M^+), 256 (M^+ − H_2O), and 201 (M^+ − CO_2Et).

(vi) *Ethyl 1-(m-nitrophenyl)-2-oxocyclopentanecarboxylate* (**5f**) was obtained by method B and column chromatography in light petroleum–ether (47:3) as an oil (0.60 g, 40%) (Found: C, 60.6; H, 5.7. $C_{14}H_{15}NO_5$ requires C, 60.6; H. 5.5%); ν_{max}(film) 1 760, 1 740, and 1 540 cm^{-1}; δ_H($CDCl_3$) 1.22 (3 H, t), 1.85–3.15 (6 H, m, 3 × CH_2), 4.22 (2 H, q), 7.53 (1 H, dt, $J_{4,5}$ and $J_{5,6}$ 8.0 Hz, $J_{2,5}$ 0.5 Hz, 5-H), 7.83 (1 H, m, 6-H), 8.16 (1 H, m, 4-H), and 8.31 (1 H, dt, $J_{2,4}$ and $J_{2,6}$ 2.0 Hz $J_{2,5}$ 0.5 Hz, 2-H); m/z 277 (M^+) 249 (M^+ − CO), 220 (M^+ − C_3H_5O), and 204 (M^+ − $CO_2C_2H_5$).

* The exchange is in fact very rapid, and in most cases a reaction time of 1 h would be sufficient.

Synthesis of p-*Trifluoromethylphenylboronic Acid* (**1b**) *and the Corresponding Boroxin.*—Butyl-lithium (1.6M solution in hexane; 27.6 ml, 44.0 mmol) was added dropwise over 5 min to a stirred solution of 4-bromo-α,α,α-trifluorotoluene (9.0 g, 40.0 mmol) in dry tetrahydrofuran (30 ml) at −78 °C under nitrogen. After 1 h, triethyl borate (6.42 g, 44.0 mmol) was added dropwise over 5 min, and the mixture was stirred at −78 °C for 1.5 h. Saturated aqueous ammonium chloride (30 ml) was added at −78 °C, and the mixture was allowed to warm to room temperature. Water (200 ml) was added, and the mixture was shaken with ether (400 ml). The ether extract was washed with saturated aqueous sodium hydrogen carbonate (200 ml) and saturated brine (200 ml), dried (Na_2SO_4), filtered, and evaporated under reduced pressure to yield a colourless solid (7.50 g). Crystallisation of this from water gave the *title compound* (**1b**) (5.31 g, 70%), m.p. 230–235 °C (decomp.); λ_{max}(EtOH) 268 and 275 nm (ε 1 000 and 850); ν_{max}(Nujol) 3 270, 1 515, and 1 400 cm^{-1}; δ_H([$^2H_6$]DMSO) 7.67 and 8.01 (4 H, AA′BB′, 3-, 5-H and 2-, 6-H respectively), and 8.36 (2 H, br, exch., 2 × OH); *m/z* 516 (M^+ for boroxin, 10%), 190 (M^+, 66%), and 189 (14%). A microanalysis was not obtained, since even an air-dried sample contained 3% (by ^1H NMR spectrum) of the trimeric cyclic anhydride, which was prepared to complete the characterisation.

The boronic acid (**1b**) (0.67 g) was heated at 170 °C and 0.75 mmHg for 2 h to produce a white powder which still contained 20% (^1H NMR spectrum) of the starting material. Dehydration was completed by heating the finely powdered material in a Kugelrohr apparatus at 200 °C at 0.75 mmHg for 3 h, and with conc. sulphuric acid (2 ml) in the second of two receiver bulbs. *Tris*(p-*trifluoromethylphenyl*)*boroxin* (0.58 g, 88%) was obtained as a colourless powder, m.p. 237–238 °C (Found: C, 49.1; H, 2.4. $C_{21}H_{12}B_3F_9O_3$ requires C, 48.9; H, 2.4%); λ_{max}(EtOH) 270 and 276 nm (ε 2 800 and 2 550); ν_{max}(Nujol) 1 505 and 1 405 cm^{-1}; δ_H([$^2H_6$]DMSO) 7.73 and 8.09 (4 H, AA′BB′, 3-, 5-H and 2-, 6-H respectively; *m/z* 517 (25%) 516 (M^+, 100), 515 (71), and 514 (24).

Preparation of the Arylboronic Acids (**1c–f**).—(i) Treatment of the appropriate aryl-lithium compound with triethyl borate, as described above for the synthesis of the boronic acid (**1b**), gave *p*-methoxyphenylboronic acid (**1c**) (86%), m.p. 202–205 °C (decomp.) (lit.,[8] 207 °C), *o*-methoxyphenylboronic acid (**1d**) (51%), m.p. 101–104 °C (lit.,[8] 105 °C), and mesitylboronic acid (**1e**) (86%) m.p. 190–192 °C (lit.,[9] 143–145 °C and 193–197 °C), all of which gave the expected ^1H NMR spectra.

(ii) Nitration of phenylboronic acid (**1a**) according to the method of Seaman and Johnson[10] afforded *m*-nitrophenylboronic acid (**1f**) (47%), m.p. 278 °C (decomp.) [lit.,[10] 275–276.5 °C (decomp.)]; δ_H([$^2H_6$]DMSO) 7.60 (1 H, t, $J_{4,5}$ and $J_{5,6}$ 8.25 Hz, 5-H), 7.90 (2 H, br, exch., 2 × OH), 7.95–8.40 (2 H, m, 4-H and 6-H), and 8.56 (1 H, m, 2-H).

Preparation of the Phenylboronic Acid Derivatives (**6**), (**7**), *and* (**8**).—(i) Dehydration of phenylboronic acid (**1a**) by the method outlined above for *p*-trifluoromethylboronic acid gave triphenylboroxin (**6**) (96%), m.p. 216–218 °C (lit.,[11] 214–216 °C); δ_H($CDCl_3$) 7.20–7.67 (9 H, m, 3-, 4-, 5-H) and 7.80–8.27 (6 H, m, 2-, 6-H).

(ii) Phenylboronic acid (**1a**) was treated with isopropyl alcohol according to the method of Torsell,[12] to yield diisopropyl phenylboronate (**7**) (33%) as a colourless oil, b.p. (Kugelrohr) 80–90 °C at 0.5 mmHg (lit.,[13] 98–101 °C at 8 mmHg); δ_H($CDCl_3$) 1.33 (12 H, d, *J* 5.7 Hz, 4 × CH_3), 4.69 (2 H, septet, *J* 5.7 Hz, 2 × CH), 7.20–7.48 (3 H, m, 3-, 4-, 5-H), and 7.48–7.74 (2 H, m, 2-, 6-H).

(iii) Phenylboronic acid (**1a**) was treated with propane-1,3-diol according to the method of Pailer and Fenzl[14] to give 2-phenyl-1,3,2-dioxaborinane (**8**) as a colourless oil, b.p. 120 °C at 25 mmHg; δ_H($CDCl_3$) 1.93 (2 H, quintet, *J* 5.5 Hz, 2 × 5-H), 4.02 (4 H, t, *J* 5.5 Hz, 2 × 4-H and 2 × 6-H), 7.05–7.45 (3 H, m, 3-, 4-, 5-H), and 7.45–7.85 (2 H, m, 2-, 6-H), which is similar to reported data.[15,16]

Preparation of p-*Phenylenediboronic Acid* (**9**) *and Its Tetrabutyl Ester* (**15**).—The method of Coutts *et al.*[17] yielded the diboronic acid (**9**) (56%) as colourless needles, m.p. >360 °C (lit.,[18] >420 °C); δ_H($CDCl_3$–[$^2H_6$]DMSO, 2:3) 7.57 (4 H, br s, exch., 4 × OH) and 7.68 (4 H, s, ArH).

The tetrabutyl ester (**15**) was prepared from the diboronic acid (**9**), by the method of Nielsen and McEwen,[18] as a moisture-sensitive colourless oil (92%); δ_H($CDCl_3$) 0.6–1.1 (12 H, m, 4 × CH_3), 1.1–1.9 (16 H, m, 8 × CH_2), 3.75–4.15 (8 H, m, 4 × OCH_2), and 7.48 (4 H, s, ArH).

Preparation of m-*Phenylenediboronic Acid* (**10**) *and its Cyclic Ester* (**18**).—The method of Coutts *et al.*,[17] with modifications of Nielsen and McEwen,[18] afforded the crude diboronic acid (**10**) as a colourless powder (55%). This material was too insoluble to obtain a satisfactory NMR spectrum and it was used in the next step without further purification.

The crude diboronic acid (**10**) (1.60 g, 9.66 mmol) and ethylene glycol (1.20 g, 19.4 mmol) were heated at reflux in anhydrous acetone (8.0 ml) under nitrogen for 4 h. The acetone and excess of ethylene glycol were evaporated off under reduced pressure, and the residue was passed in chloroform through a column of neutral alumina (1 g). Evaporation of the chloroform gave m-*phenylene*-2,2′-*bis*(1,3,2-*dioxaborolane*) (**18**) (1.55 g, 74%) as colourless crystals, m.p. 127–128.5 °C (from ethyl acetate–light petroleum) (Found: C, 55.0; H, 5.8. $C_{10}H_{12}B_2O_4$ requires C, 55.1; H, 5.6%); λ_{max}(dioxane) 232, 274, and 280 nm (ε 2 250, 650, and 600); ν_{max}($CHCl_3$) 1 604, 1 491, 1 481, 1 397, 1 369, 1 325, 1 320, and 1 308 cm^{-1}; δ_H($CDCl_3$) 4.38 (8 H, s, 4 × OCH_2), 7.40 (1 H, dt, $J_{4,5}$ 7.5 Hz, $J_{2,5}$ 0.7 Hz, 5-H), 7.92 (2 H, dd, $J_{4,5}$ 7.5 Hz, $J_{2,4}$ 1.4 Hz, 4-, 6-H), 8.31 (1 H, narrow m, 2-H); *m/z* 219 (11%), 218 (100), and 217 (45).

Preparation of p-*Phenylenebis*(*tributylstannane*) (**13**).—A solution of *p*-dibromobenzene (23.6 g, 0.1 mol) in dry ether (100 ml) was added over 1 h to a mixture of tributyltin chloride (81.4 g, 0.25 mol) and magnesium (6.08 g, 0.25 mol) in dry ether (75 ml), which was heated at reflux, and the mixture was refluxed for a further 23 h. The mixture was cooled to 5 °C and shaken with ice-cold hydrochloric acid (2.5M; 125 ml). The ether layer was separated, washed with saturated brine (90 ml), dried (Na_2SO_4), and evaporated. The residue was distilled to yield the *title compound* (**13**) as a colourless oil (17.5 g, 27%), b.p. 206–210 °C at 0.04 mmHg (lit.,[7] 155 °C at 5 mmHg, see Discussion) (Found: C, 54.5; H, 9.3. Calc. for $C_{30}H_{58}Sn_2$: C, 54.9; H, 8.9%); λ_{max}(cyclohexane) 229 nm (ε 21 300); δ_H($CDCl_3$) 0.89 (18 H, t, 6 × CH_3), 1.05 (12 H, t, 6 × CH_2Sn), 1.34 (12 H, m, 6 × CH_2) 1.57 (12 H, m, 6 × CH_2) 7.44 (4 H, narrow m, ^{117}Sn and ^{119}Sn satellites were unresolved and gave *J* 17 Hz, 34 Hz, and 50 Hz.

Reaction of p-*Phenylenebis*(*tributylstannane*) (**13**) *with Lead Tetra-acetate.*—The distannane (**13**) (1.31 g, 2.0 mmol) was added to a stirred mixture of lead tetra-acetate (0.976 g, 2.2 mmol) and mercury(II) acetate (0.035 g, 0.11 mmol) in chloroform (3.3 ml) at 40 °C. The mixture was stirred at 40 °C for 21 h, when the test for lead tetra-acetate was negative, and then filtered through Celite, which was washed with chloroform (10 ml). The filtrate was evaporated to give a brown semi-solid residue (2.35 g). This was dissolved in chloroform (1 ml), and acetic acid was added dropwise until the yellow colour was removed (4 drops); the solution was then stirred for 15 min. Dry pentane (10 ml) was added and impure *p*-

(tributylstannyl)phenyl–lead triacetate (**14**) was collected by means of a centrifuge as a fine powder (15 mg); $\delta_H(CDCl_3)$ 0.88 (9 H, t, 3 × CH_3), 1.08 (6 H, m, 3 × CH_2), 1.34 (6 H, m, 3 × CH_2), 1.50 (6 H, m, 3 × CH_2), 2.10 (9 H, s, 3 × OAc), 7.56 and 7.65 (4 H, AA'BB', ^{207}Pb satellites gave $J_{2,Pb}$ 396 Hz and $J_{3,Pb}$ 202 Hz, 2-, 6-H and 3-, 5-H respectively).

Preparation of 2,2,2',2',5,5'-*Hexamethyl*-p-*phenylene*-5,5'-*bis*-(1,3-*dioxane*-4,6-*dione*) (**17**).—(i) *p*-Phenylenediboronic acid (**9**) (1.094 g, 6.6 mmol) was added over 5 min to a stirred mixture of lead tetra-acetate (5.85 g, 13.2 mmol) and mercury(II) acetate (0.841 g, 2.64 mmol) in chloroform (20 ml) at 60 °C, and the mixture was stirred at 60 °C for 43 h. The mixture was cooled in ice, and a slurry of the Meldrum's acid derivative (**16**) (3.13 g, 19.8 mmol) in pyridine (3.16 g, 40 mmol) was added with stirring. The mixture was then stirred at 60 °C for 16 h.

The mixture was cooled to room temperature, diluted with chloroform (60 ml), and shaken with sulphuric acid (3M; 30 ml). The emulsion was filtered at the pump, and the filter was washed with chloroform (2 × 20 ml). The two phases of the filtrate were separated, and the aqueous layer was washed with chloroform (20 ml). The combined chloroform extracts were cooled to 0 °C, shaken briefly with ice-cold aqueous sodium hydroxide (3M; 75 ml), washed with saturated brine (75 ml), dried (Na_2SO_4), and evaporated to give a solid (1.76 g). The crude product was triturated with cold ether (2 × 20 ml) to give the *title compound* (**17**) (1.16 g, 45%) as colourless needles (from chloroform–light petroleum), m.p. 212–213 °C (Found: C, 61.2; H, 5.4. $C_{20}H_{22}O_8$ requires C, 61.5; H, 5.7%); λ_{max}(dioxane) 233 nm (ε 5 300); $\nu_{max}(CHCl_3)$ 1 779 and 1 743 cm^{-1}; $\delta_H(CDCl_3)$ 1.32 (6 H, s, 2 × CH_3), 1.75 (6 H, s, 2 × CH_3), 1.89 (6 H, s, 2 × CH_3), and 7.49 (4 H, s, ArH); *m/z* 390 (M^+, 2%), 288 ($M - C_4H_6O_3$, 62), and 186 ($M - C_8H_{12}O_6$, 100).

(ii) Tetrabutyl *p*-phenylenediboronate (**15**) (0.18 g, 2.0 mmol) was added dropwise by syringe to a stirred mixture of lead tetra-acetate (1.418 g, 3.2 mmol) and mercury(II) acetate (0.12 g, 0.32 mmol) in chloroform (4.8 ml) under dry nitrogen at 60 °C, and the mixture was stirred overnight at 60 °C. The solution was cooled in ice, and the Meldrum's acid derivative (**16**) (0.76 g, 4.8 mmol) in warmed pyridine (0.79 g, 10.0 mmol) was added. The mixture was stirred at 60 °C and worked up as in (i) above to give compound (**17**) (0.306 g, 49%), m.p. 212–213 °C, identical (by ^{1}H NMR spectrum) with the above material.

Preparation of 2,2,2',2',5,5'-*Hexamethyl*-m-*phenylene*-5,5'-*bis*-(1,3-*dioxane*-4,6-*dione*)(**19**).—*m*-Phenylene-2,2'-bis(1,3,2-dioxaborolane) (**18**) (1.09 g, 5.0 mmol) was added over 3 min to a stirred mixture of lead tetra-acetate (4.43 g, 10.0 mmol) and mercury(II) acetate (0.319 g, 1.0 mmol) in chloroform (15 ml) at 60 °C, and the mixture was stirred at 60 °C for 21 h. The mixture was cooled in ice, and a slurry of the Meldrum's acid derivative (**16**) (1.58 g, 10.0 mmol) in pyridine (2.37 g, 30.0 mmol) was added with stirring. The temperature was raised to 60 °C and the mixture was stirred at this temperature overnight.

The reaction was worked up as in the synthesis of compound (**17**) above to give the crude product (1.10 g). This material was triturated with ice-cold ether (2 × 10 ml) to give the *title compound* (**19**) (0.85 g, 44%), m.p. 170–171 °C (from chloroform–light petroleum) (Found: C, 61.3; H, 5.6. $C_{20}H_{22}O_8$ requires C, 61.5; H, 5.7%); λ_{max}(dioxane) 230 nm (ε 2 300); $\nu_{max}(CHCl_3)$ 1 778 and 1 744 cm^{-1}; $\delta_H(CDCl_3)$ 1.40 (6 H, s, 2 × CH_3), 1.77 (6 H, s, 2 × CH_3), 1.93 (6 H, s, 2 × CH_3), 7.45–7.50 (3 H, m, 4-, 5-, 6-H), and 7.50–7.54 (1 H, m, 2-H); *m/z* 288 ($M - C_4H_6O_3$, 100%) and 186 ($M - C_8H_{12}O_6$, 100).

General Method for Synthesis of Aryl–lead Triacetates by Boron–Lead Exchange.—The arylboronic acid (10.0 mmol) was added over 15 min to a stirred mixture of lead tetra-acetate (4.43 g, 10.0 mmol) and mercury(II) acetate (0.5 or 1.0 mmol) in chloroform (15.2 ml) at 40 °C. The mixture was stirred at 40 °C for 1 h and then at room temperature overnight. The reaction mixture was filtered through Celite, which was then washed with chloroform (2 × 30 ml). The chloroform filtrate was washed with water (40 ml), and the aqueous layer was then extracted with chloroform (2 × 80 ml). The combined chloroform solutions were filtered through Celite and then concentrated to a volume of 100 ml at 40 °C. Light petroleum (600 ml) was added and the mixture was kept at 0 °C overnight. Crystals of the aryl–lead triacetate were deposited and collected at the pump.

The following aryl–lead triacetates were produced by the above method. (i) Phenyl–lead triacetate (**2**) (2.84 g, 62%) was obtained by use of mercury acetate (0.5 mmol) as colourless crystals, m.p. 102–103 °C (lit.,[19] 103–105 °C); $\delta_H(CDCl_3)$ 2.10 (9 H, s, 3 × CH_3) and 7.25–7.75 (5 H, m, ^{207}Pb satellites gave $J_{2,Pb}$ 372 Hz, $J_{3,Pb}$ 168 Hz, ArH) which is similar to that previously reported.[20]

(ii) *p*-Trifluoromethylphenyl–lead triacetate (**20**) (3.48 g), obtained by use of mercury acetate (1.0 mmol), contained a substantial amount of oligomer (^{1}H NMR spectroscopy). The crude material was stirred in a mixture of acetic acid (40 ml) and chloroform (40 ml) for 0.5 h. The chloroform solution was washed with water (2 × 40 ml), dried (Na_2SO_4), concentrated to a volume of 20 ml and light petroleum (200 ml) was added. Crystallisation at 0 °C gave the pure lead compound (**20**) (2.00 g, 38%), m.p. 206–210 °C (decomp.) [lit.,[3] 198–200 °C (decomp.)], identical by ^{1}H NMR spectrum with authentic material.[3]

(iii) *p*-Methoxyphenyl–lead triacetate (**21**) was obtained by use of mercury acetate (1.0 mmol). The crude material contained oligomer, and was treated as in (ii) above to give the monomer (**21**) (1.64 g, 33%), m.p. 130–134 °C (lit.,[21] 138–139 °C), ^{1}H NMR spectrum identical with reported data.[20]

(iv) *o*-Methoxyphenyl–lead triacetate (**22**) was obtained by use of mercury acetate (0.5 mmol) as pale yellow crystals (3.64 g, 74%), m.p. 158–160 °C (lit.,[4] 148–151 °C), identical by ^{1}H NMR spectrum with authentic material.[4]

(v) *Mesityl–lead triacetate* (**23**) was obtained [mercury acetate (0.5 mmol) and acetic acid treatment of the crude product as in (ii) above] as pale yellow crystals (2.24 g, 44%), m.p. 130–132 °C and 196–198 °C (Found: C, 35.9; H, 4.3. $C_{15}H_{20}O_6Pb$ requires C, 35.8; H, 4.0%); λ_{max}(EtOH) 230sh and 260sh (ε 1 200 and 550); ν_{max}(Nujol) 1 550 cm^{-1}; $\delta_H(CDCl_3)$ 2.02 (9 H, s, 3 × OAc), 2.24 (3 H, s, ^{207}Pb satellites gave $J_{Me,Pb}$ 20.6 Hz, CH_3), 2.54 (6 H, s, ^{207}Pb satellites gave $J_{Me,Pb}$ 33.4 Hz, 2 × CH_3), and 7.00 (2 H, s, ^{207}Pb satellites gave $J_{3,Pb}$ 176.7 Hz, 3-, 5-H).

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References

1 D. J. Ackland and J. T. Pinhey, *J. Chem. Soc., Perkin Trans. 1*, 1987, 2695.
2 R. P. Kozyrod and J. T. Pinhey, *Aust. J. Chem.*, 1985, **38**, 1155 and reference therein.
3 H. C. Bell, J. R. Kalman, J. T. Pinhey, and S. Sternhell, *Aust. J. Chem.*, 1979, **32**, 1521.
4 R. P. Kozyrod, J. Morgan, and J. T. Pinhey, *Aust. J. Chem.*, 1985, **38**, 1147.
5 R. C. Larock, 'Organomercury Compounds in Organic Synthesis,' Springer-Verlag, Berlin, 1985, p. 15.

6 J. T. Pinhey and B. A. Rowe, *Aust. J. Chem.*, 1980, **33**, 113.
7 K. L. Jaura, H. S. Hundal, and R. D. Handa, *Indian J. Chem.*, 1967, **5**, 211.
8 W. Konig and W. Scharrnbeck, *J. Prakt. Chem.*, 1930, **128**, 153.
9 M. F. Hawthorne, *J. Org. Chem.*, 1958, **23**, 1579.
10 W. Seaman and J. R. Johnson, *J. Am. Chem. Soc.*, 1931, **53**, 711.
11 R. M. Washburn, E. Levens, C. F. Albright, and F. A. Billig, *Org. Synth.*, 1959, **39**, 3.
12 K. Torsell, *Acta Chem. Scand.*, 1954, **8**, 1779.
13 H. C. Brown and T. E. Cole, *Organometallics*, 1983, **2**, 1316.
14 M. Pailer and W. Fenzl, *Monatsh. Chem.*, 1961, **92**, 1294.
15 F. A. Davis, I. J. Turchi, B. E. Maryanoff, and R. O. Hutchins, *J. Org. Chem.*, 1972, **37**, 1583.
16 O. Exner and R. Bose, *Collect. Czech. Chem. Commun.*, 1974, **39**, 2234.
17 I. G. C. Coutts, H. R. Goldschmid, and O. C. Musgrave, *J. Chem. Soc. C*, 1970, 488.
18 D. R. Nielsen and W. E. McEwen, *J. Am. Chem. Soc.*, 1957, **79**, 3081.
19 R. Criegee, P. Dimroth, and R. Schempf, *Chem. Ber.*, 1957, **90**, 1337.
20 D. de Vos, H. O. van der Kooi, J. Walters, and A. van der Gen, *Recl. Trav. Chim. Pays-Bas.*, 1975, **94**, 94.
21 R. P. Kozyrod and J. T. Pinhey, *Org. Synth.*, 1984, **62**, 24.

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