Polyfunctionalized Aryllead Triacetates in a Cascade Synthesis of Tetracyclic Isochromanocoumarin-Type Compounds

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Abstract: The three-step one-pot α-arylation-annulation sequence leading to the reaction of 4-hydroxycoumarins with in situ generated 2-(bromomethyl)aryllead triacetates carried out in the presence of a combination of *ortho*-phenantroline–potassium *tert*-butoxide afforded tetracyclic benzo[*b*]pyran compounds in good to high yields.

Key words: 4-hydroxycoumarins, arylboronic acids, aryllead triacetates, reductive ligand coupling reactions

Coumarins are an important class of benzopyrones widely distributed in nature as individual compounds, as well as being the constituent of the skeleton of more complex natural molecules, exhibiting a broad range of biological activities.[1] In this paper we report the synthesis of the new polymethoxy-substituted tetracyclic 6*H*,11*H*-[2]benzopyrano-[4,3-*c*][1]benzopyran-11-one **1**, constructed by a combination of coumarin and 1*H*-2-benzopyran structural subunits (Figure 1). Being isostructural analogs of a number of pharmacologically active naturally occurring molecules, compounds of type **1** can potentially present a range of biologically useful properties. For example, the benzazepine kenpaullone analog **2** is an effective anti-tumor agent towards 60 human cancer cell lines.[2] The natural pyranocoumarins of the alloxanthoxyletin type[3] **3** display a wide range of pharmacological actions including anticancer[4] and anti-HIV activity.[5] Belonging to the same family of organic compounds, dihydropyranocoumarins can act as therapeutic agents for neurodegenerative diseases (for example Alzheimer Disease).[6] Finally, wedelolactone **4** – the tetracyclic natural product formed by polyoxygenated coumarin and benzofuran units is used as a venomous snake-bite antidote.[7]

Among the various strategies that can be used for the synthesis of benzopyran compounds,[8–13] some recent ones rely on methodologies developed in our group, involving

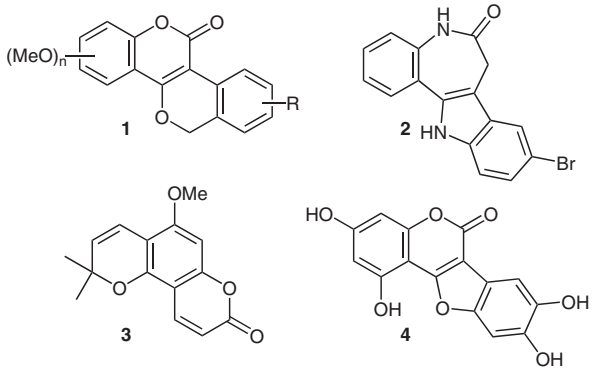

Figure 1

application of three-step one-pot organobismuth[12] or organolead-mediated[13] α-arylation-annulation sequence.

These methods were efficient for the synthesis of dibenzo[*b*,*d*]pyran compounds, derived from phenols leading to 60–65% overall yields of cyclization product. On the other hand, the extension of this methodology to β-ketoester or β-ketolactone derivatives afforded only poor yields of the annulation products. Therefore, the aim of this work was the adaptation of the organolead-mediated cascade cyclization strategy[13] to the synthesis of heterocyclic products derived from the naturally occurring β-ketolactones **7a–d**.[14]

The synthesis of type **1** tetracyclic derivatives implies a three-step one-pot sequence of reactions presented in Scheme 1. Transmetallation between arylboronic acids **5a**,**b** and lead tetraacetate performed in the presence of a catalytic amount of mercuric acetate according to Pinhey's procedure[15] afforded the aryllead triacetates **6a**,**b**, which were treated directly with 4-hydroxycoumarins **7a–d** in the presence of a base (Figure 2). This step involves a reductive ligand coupling[16] C-arylation reaction, which is realized by aryl derivatives of lead,[17] bismuth,[17a,b,18] iodine,[17a,b,19] and some other heteroatoms.[17a,b] These processes are considered to take place with formation of a covalent arylheteroatom-substrate intermediate **8**, that subsequently undergoes a reductive-elimination-type

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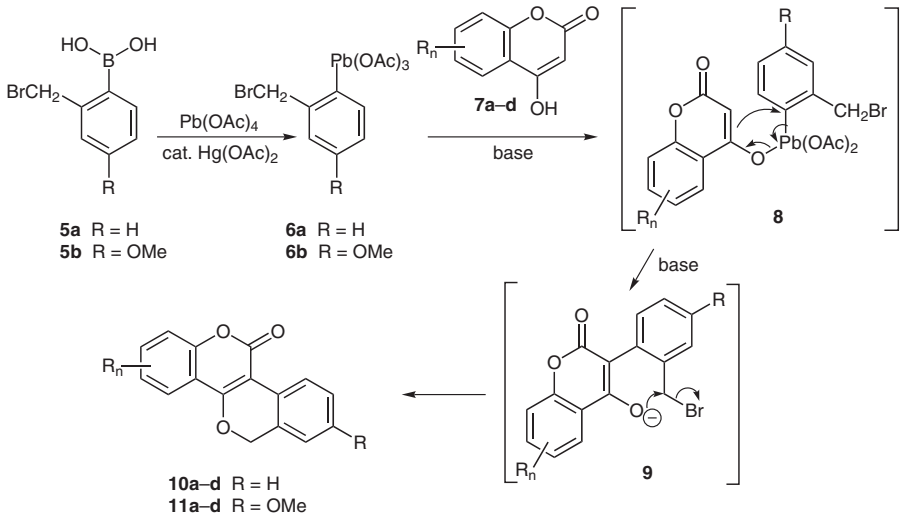
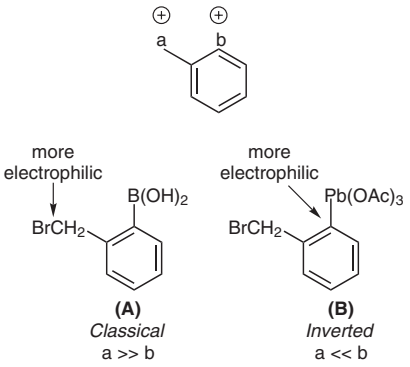


Scheme 1 Organolead-mediated arylation-annulation reaction

reaction[20] to afford the α-arylation product **9**. Finally spontaneous intramolecular cyclization leads to the tetracyclic products **10**,**11a–d** (Scheme 1).

This transmetallation procedure presented in Scheme 1 allows reactivity umpolung of the system (**A**) with an aromatic electrophilic center less reactive than the benzylic electrophilic center towards nucleophilic reagents[21,22] into the system (**B**) with the aromatic center more reactive towards nucleophiles (Scheme 2). Indeed, the presence of a halogen atom in the coordination sphere of the lead atom in **6a** and **6b** does not significantly alter the usual reactivity of aryllead triacetates towards soft nucleophiles.

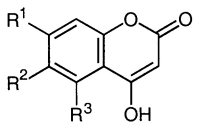


Scheme 2

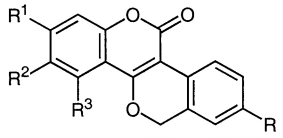
When the classical conditions of Barton's arylation of 4-hydroxycoumarin derivatives with aryllead triacetates[14b,c,23] were used with the lead compound **6a** obtained by the three-step one-pot methodology, described in Scheme 1 [4-hydroxycoumarin **7a** or **7b**, aryllead triacetate **6a** (1.1 equiv), pyridine (3 equiv) at 45 °C in $CHCl_3$], only poor yields of the tetracyclic products **10a** and **10b** (Figure 2, Table 1, entry 1) were obtained. Increasing the amount of pyridine to six equivalents in order to neutralize the bromhydric acid formed in the cyclization step did not improve the yields of annulation products. This can be explained as pyridine does not function only as a base. In the case of organolead-mediated C-arylation reactions, it was suggested that pyridine acts as a ligand donor rather than as a base.[24] Moreover, Moloney's results[25] as well as our recent studies[13] showed that the nature of the base (or additive) can strongly affect the yields and kinetics of the organolead-mediated reductive coupling reactions. However, the origin of these effects remains unclear. To improve the yields of the annulation products **10/11a–d**, and to get a better understanding of the origin of the influence of the nature of the base, the arylation reactions were carried out in the presence of different bases: Et_3N, *N*,*N*,*N*′,*N*′-tetramethylguanidine (TMG), *ortho*-phenanthroline (*o*-phen), or a combination of bases, pyridine–Et_3N, pyridine–DMAP and *o*-phen–*t*-BuOK.

Application of Et_3N and TMG, the most effective bases in the case of the organobismuth-mediated C-arylation reactions,[17a,18] led only to traces of the desired products (Table 1, entries 2 and 3). However, when a stronger base (Et_3N) was added to pyridine, significant improvement of the yields was observed (Table 1, entry 4).

The same results were obtained when the binary system pyridine–DMAP was used (Table 1, entry 5). As these facts agree with the idea of a specific ligating role of pyridine and related compounds in the coordinating sphere of lead,[24] *ortho*-phenantroline, a frequently used bidentate ligand, was employed as an additive. This led to a noticeable increase in the overall yields of cyclization products to 33–41%, in the case of arylation of polymethoxy-substituted 4-hydroxycoumarins **7b–d**, and to 58% yield when non-substituted coumarin **7a** was used (Table 1, entry 6). Finally, the pair of bases [*o*-phen–*t*-BuOK (3:1)] appeared as the best combination of additives with the overall yield of annulation product reaching 76% in the case of reaction with coumarin **7a** (Table 1, entry 7). The use of this last system of additives with aryllead triacetate **6b** gave the tetracyclic products **11a–d** in 51%, 39%, 44%, and 31% yields respectively.



	R^1	R^2	R^3
7a	H	H	H
7b	MeO	H	MeO
7c	MeO	MeO	H
7d	MeO	MeO	MeO



	R	R^1	R^2	R^3
10a	H	H	H	H
10b	H	MeO	H	MeO
10c	H	MeO	MeO	H
10d	H	MeO	MeO	MeO
11a	MeO	H	H	H
11b	MeO	MeO	H	MeO
11c	MeO	MeO	MeO	H
11d	MeO	MeO	MeO	MeO

Figure 2

Table 1 Influence of the Additives on the Three-Step One-Pot Synthesis of the Annulation Products **10a–d**, Using in situ Generated 2-(Bromomethyl)phenyllead Triacetate (**6a**)

Entry	Additives (equiv)[a,b]	Overall Yields of the Three-Step Sequence (%)			
		10a	**10b**	**10c**	**10d**
1	Pyridine (3)	15	11	–	–
2	Et_3N (3)	traces	traces	–	–
3	TMG (3)	traces	traces	–	–
4	Pyridine–Et_3N (3:3)	24	25	18	11
5	Pyridine–DMAP (3:3)	20	23	–	–
6	*o*-Phen (3)	58	34	41	33
7	*o*-Phen–*t*-BuOK (3:1)	76	45	47	47

[a] The ratios between the reagents were: substrate **7a–d** –arylboronic acid–additives, 1:1.2:x.
[b] TMG = *N*,*N*,*N*′,*N*′-tetramethylguanidine, *o*-Phen = *ortho*-phenanthroline.

It is postulated that the application of bidentate ligand like *ortho*-phenantroline can change the saturation of the coordinating sphere of the non-transition element, consequently displacing the equilibrium between the monomeric and oligomeric forms of the organolead compound to the most reactive monomeric state of reagent. The same effect can be observed when the bulky chiral bases are used in the enantioselective organolead-mediated C-arylation reactions.[26] Moreover, incorporation of the additional ligand into the coordinating sphere of the lead atom can strongly increase the solubility of polar intermediate **8** in chloroform, which undoubtedly can influence the kinetics of the coupling process. The role of the second additive, potassium *tert*-butoxide, can be to neutralize the bromhydric acid formed during the cyclization (Figure 3), that can otherwise react with the organolead reagent.

The decrease of the yields of the annulation products **10b–d** (45–47%) in the reactions of the polymethoxy-substituted 4-hydroxycoumarins **7b–d** in comparison with the unsubstituted analog **10a** (76%) is noteworthy, as the influence of the A-ring methoxy substitution was not significant when compared with simpler aryllead reagents.[17]

Moreover, the yields of 4′-methoxy products **11a–d** were also lower than those obtained with the unsubstituted tetracyclic compounds **10a–d**. This fact is surprising, as organolead-mediated C-arylation reactions are especially powerful for the incorporation of highly electron rich aryl fragments into organic substrates.[17]

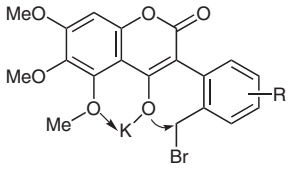


Figure 3

These effects could be attributed to a complexation of the intermediate potassium cation with a number of donor oxygen atoms reducing the nucleophilic character of the oxygen center involved in the final cyclization. Increasing the amount of *t*-BuOK resulted in the formation of a number of by-products. Use of other solvents, more tolerant to the presence of strong bases (THF, toluene, benzene, Et_2O) did not improve the yields of annulation products.

In conclusion, the three-step one-pot organolead-mediated arylation-annulation sequence was successfully used for the synthesis of tetracyclic 6*H*,11*H*-[2]benzopyrano[4,3-*c*][1]benzopyran-11-ones derived from 4-hydroxycoumarin compounds. The study of their biological properties is now under investigation.

Melting points were recorded with a Büchi capillary apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were obtained with Bruker AC-200P spectrometer. Chemical shifts (δ) are reported in ppm for a solution of a compound in $CDCl_3$ with $SiMe_4$ as internal reference. Separations by column chromatography (CC) were performed using Merck Kieselgel 60 (70–230 mesh). All solvents were purified by standard techniques. 2-(Bromomethyl)phenylboronic acid **5a** was synthesized as previously reported.[22] All commercially available reagents were obtained from Lancaster and used without further purification.

2-(Bromomethyl)-4-methoxyphenylboronic Acid (5b)

A mixture of 2-methyl-4-methoxyphenylboronic acid (2.90 g, 18.0 mmol), NBS (3.4 g, 18.9 mmol), and benzoyl peroxide (1.37 g, 5.7 mmol) in CCl_4 (150 mL) was refluxed for 2 h under irradiation with an incandescent lamp (300 W). Then the reaction mixture was

cooled to 50 °C and twice filtered through a porous glass filter. The reaction product was washed with cold Et_2O (30 mL) and recrystallized from CH_2Cl_2–Et_2O–hexane to afford **5b** (2.1 g, 48%) as a white solid; mp 135 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.89 (s, 3 H), 5.09 (s, 2 H), 6.95–7.02 (m, 2 H), 8.32 (d, 1 H, *J* = 8.6 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 33.6, 55.3, 113.4, 116.8, 140.0, 140.2, 147.5, 163.0.

Anal. Calcd for $C_8H_{10}BBrO_3$ (244.87): C, 39.24; H, 4.12. Found: C, 39.48; H, 3.89.

Three-Step One-Pot Organolead-Mediated Arylation–Annulation Sequence; Typical Procedure

A solution of 2-(bromomethyl)phenylboronic acid **5a** (0.054 g, 0.25 mmol) in anhyd $CHCl_3$ (1 mL) was added to a mixture of $Pb(OAc)_4$ (0.111 g, 0.25 mmol) and $Hg(OAc)_2$ (0.008 g, 0.025 mmol) in $CHCl_3$ (1.5 mL) at 40 °C under an inert gas. The mixture was stirred at 40 °C for 1 h, then at r.t. overnight. *t*-BuOK (0.02 g, 0.21 mmol), the solution of 4-hydroxychromen-2-one **7a** (0.034 g, 0.21 mmol) and *o*-phenanthroline (0.112 g, 0.62 mmol) in anhyd $CHCl_3$ (1.5 mL) were added. The reaction mixture was stirred at 45 °C for 4 h, and then at r.t. overnight. The solvent was distilled under reduced pressure and the residue was purified by column chromatography on silica gel (pentane–Et_2O, 1:1) to afford the annulation product **10a** (0.040 g, 76%) as a slightly yellow powder; mp 154 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.41 (s, 2 H), 7.13 (d, 1 H, *J* = 7.2 Hz), 7.27–7.48 (m, 4 H), 7.57 (t, 1 H, *J* = 7.6 Hz), 7.87 (d, 1 H, *J* = 7.8 Hz), 8.55 (d, 1 H, *J* = 7.6 Hz).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 69.7, 102.6, 115.2, 116.5, 123.1, 123.9, 124.0, 124.9, 126.6, 127.4, 128.2, 129.0, 132.5, 152.9, 160.1, 161.2.

Anal. Calcd for $C_{16}H_{10}O_3$ (250.25): C, 76.79; H, 4.03. Found: C, 76.85; H, 4.09.

Compound 10b

Column chromatography (Et_2O) gave a white solid (45%); mp 205 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.84 (s, 3 H), 3.87 (s, 3 H), 5.28 (s, 2 H), 6.29 (d, 1 H, *J* = 2.3 Hz), 6.43 (d, 1 H, *J* = 2.3 Hz), 7.09 (d, 1 H, *J* = 7.3 Hz), 7.27 (dt, 1 H, *J* = 7.3, 1.1 Hz), 7.38 (dt, 1 H, *J* = 7.9, 1.3 Hz), 8.46 (d, 1 H, *J* = 7.6 Hz).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.7, 56.3, 69.6, 93.0, 96.0, 99.7, 99.8, 123.6, 124.4, 127.0, 127.3, 128.8, 156.4, 158.8, 160.2, 163.5, 164.1.

Anal. Calcd for $C_{18}H_{14}O_5$ (310.31): C, 69.67; H, 4.55. Found: C, 69.48; H, 4.39.

Compound 10c

Column chromatography (EtOAc–pentane, 3:7) gave a slightly yellow solid (47%); mp 158 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.96 (s, 6 H), 5.38 (s, 2 H), 6.84 (s, 1 H), 7.21 (s, 1 H), 7.26–7.41 (m, 3 H), 8.56 (d, 1 H, *J* = 7.6 Hz).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 56.3, 56.4, 69.7, 99.5, 100.4, 103.1, 107.2, 123.8, 124.5, 127.0, 127.7, 129.0, 146.4, 149.0, 153.6, 159.6, 160.6, 161.4.

Anal. Calcd for $C_{18}H_{14}O_5$ (310.31): C, 69.67; H, 4.55. Found: C, 69.81; H, 4.67.

Compound 10d

Column chromatography (Et_2O) gave a slightly yellow solid (47%); mp 152 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.88 (s, 3 H), 3.92 (s, 3 H), 3.93 (s, 3 H), 5.69 (s, 2 H), 7.12 (d, 1 H, *J* = 7.2 Hz), 7.29–7.44 (m, 3 H), 8.46 (d, 1 H, *J* = 7.0 Hz).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 56.3, 61.4, 62.3, 69.8, 96.3, 100.9, 103.4, 123.7, 124.6, 127.0, 127.1, 127.7, 128.9, 140.2, 150.8, 150.9, 157.2, 160.1, 162.9.

Anal. Calcd for $C_{19}H_{16}O_6$ (340.33): C, 67.06; H, 4.74. Found: C, 67.26; H, 4.51.

Compound 11a

Column chromatography (Et_2O–pentane, 1:1) gave a white solid (51%); mp 137 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.85 (s, 3 H), 5.37 (s, 2 H), 6.67 (d, 1 H, *J* = 2.4 Hz), 6.94 (dd, 1 H, *J* = 8.9, 2.4 Hz), 7.27–2.38 (m, 2 H), 7.54 (dt, 1 H, *J* = 7.9, 1.4 Hz), 7.84 (d, 1 H, *J* = 7.8 Hz), 8.50 (d, 1 H, *J* = 8.6 Hz).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.4, 69.6, 102.8, 110.2, 113.5, 116.5, 122.9, 123.6, 124.0, 124.7, 126.6, 129.3, 132.0, 152.5, 159.6, 159.7, 161.4.

Anal. Calcd for $C_{17}H_{12}O_4$ (280.27): C, 72.85; H, 4.32. Found: C, 72.61; H, 4.72.

Compound 11b

Column chromatography (EtOAc–pentane, 1:1) gave a white solid (39%); mp 183 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.83 (s, 3 H), 3.94 (s, 6 H), 5.33 (s, 2 H), 6.64 (d, 1 H, *J* = 2.6 Hz), 6.82 (d, 1 H, *J* = 2.6 Hz), 6.92 (dd, 1 H, *J* = 8.8, 2.8 Hz), 7.18 (s, 1 H), 8.47 (d, 1 H, *J* = 8.8 Hz).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.3, 56.3, 56.3, 69.5, 99.5, 100.4, 102.9, 107.4, 110.1, 113.4, 119.5, 126.2, 128.8, 146.3, 148.5, 153.1, 159.2, 159.9, 160.7.

Anal. Calcd for $C_{19}H_{16}O_6$ (340.33): C, 67.06; H, 4.74. Found: C, 66.94; H, 4.96.

Compound 11c

Column chromatography (EtOAc–pentane, 1:1) gave a white solid (44%); mp 207 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.83 (s, 3 H), 3.94 (s, 6 H), 5.33 (s, 2 H), 6.64 (d, 1 H, *J* = 2.6 Hz), 6.82 (s, 1 H), 6.91 (dd, 1 H, *J* = 8.8, 2.8 Hz), 7.18 (s, 1 H), 8.47 (d, 1 H, *J* = 8.8 Hz).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.4, 56.3, 56.4, 69.6, 99.5, 100.4, 102.9, 107.4, 110.1, 113.4, 119.5, 126.2, 128.9, 146.3, 148.6, 153.2, 159.3, 159.9, 160.8.

Anal. Calcd for $C_{19}H_{16}O_6$ (340.33): C, 67.06; H, 4.74. Found: C, 67.31; H, 4.62.

Compound 11d

Column chromatography (EtOAc–pentane, 1:1) gave a white solid (31%); mp 137 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.84 (s, 3 H), 3.88 (s, 3 H), 3.91 (s, 6 H), 5.32 (s, 2 H), 6.65–6.80 (m, 2 H), 6.91 (dd, 1 H, *J* = 8.8, 2.6 Hz), 8.43 (d, 1 H, *J* = 8.8 Hz).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.4, 56.3, 61.4, 62.3, 69.7, 96.3, 96.6, 109.9, 111.4, 113.6, 119.6, 126.4, 129.2, 148.7, 150.4, 150.7, 156.8, 159.5, 160.3, 161.3.

Anal. Calcd for $C_{20}H_{18}O_7$ (370.35): C, 64.86; H, 4.90. Found: C, 64.57; H, 5.11.

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