Synthesis of 2-Aryl- and 2-Heteroaryl-3,5-dimethoxy-1,4-benzoquinones Involving Pd-Catalyzed Cross-Coupling of (2,3,4,6-Tetramethoxyphenyl)boronic Acid

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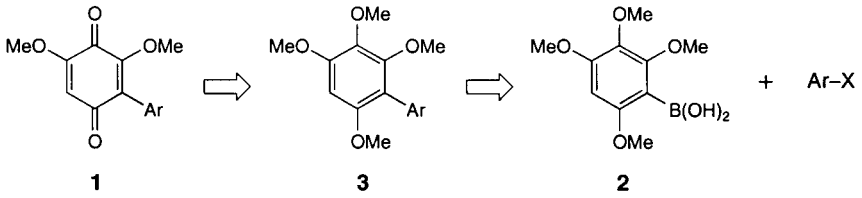
A series of 2-aryl- and 2-heteroaryl-substituted 3,5-dimethoxy-1,4-benzoquinones (compounds **27**–**36**) have been synthesized by cross-coupling of (2,3,4,6-tetramethoxyphenyl)boronic acid (**2**) with aromatic bromides or iodides in the presence of $[Pd^0(Ph_3)_4]$ and Na_2CO_3, followed by AgO-promoted oxidation of the resulting biaryl compounds **17**–**26**.

Introduction. – Quinone-type compounds occupy a special place among a variety of natural and synthetic agents with biological activity, standing out both as primary and secondary metabolites [1–4], which justifies the study of their reactivity. Thus, it is important to search for simple, but powerful, methods for the synthesis of substituted quinones, in particular of methoxyaryl-substituted benzoquinones. Most synthetic routes to substituted quinones are based on the elaboration of a pre-existing aromatic or heteroaromatic core. Aryl-substituted quinones have been prepared, *e.g.*, by direct C–C bond-formation on the quinone nucleus by means of Pd-catalyzed cross-coupling [5]. *Liebeskind* and *Riesinger* [6] reported a general and high-yielding route to a variety of aryl- and heteroaryl-substituted quinones *via* the Pd–Cu co-catalyzed cross-coupling of stannyl quinones with aryl and heteroaryl iodides. More recently, *Davies et al.* [7] reported the synthesis and reactivity of quinone-type boronic-ester derivatives *via* a highly regioselective *Dötz* annulation of *Fischer* carbene complexes with alkylboronates. Additionally, these compounds were submitted to Pd-catalyzed coupling with various aryl halides, leading to highly substituted quinones.

Despite the large number of substances containing oxygenated aromatic rings with biological activity in nature [8], there are only few methods to prepare methoxyaryl-substituted benzoquinone derivatives. The selective arylation of 2-methoxy-1,4-benzoquinone was reported by *Engler* and *Reddy* [9] as part of their studies of the γ-silyl effect in $TiCl_4$-catalyzed arylation of 1,4-benzoquinones. *Higuchi et al.* reported selective quinone formation *via* oxidation of tetramethoxy-1,1′-biphenyls with the Ru(por)-2,6-disubstituted pyridine *N*-oxide system in the presence of acid [10].

Based on our earlier studies [11–13], and, after failing to obtain 2-aryl-3,5-dimethoxy-1,4-benzoquinones (**1**) directly from 2,6-dimethoxy-1,4-benzoquinone [14], a retrosynthetic analysis for this class of compounds was elaborated (*Scheme 1*). The idea was to establish a C–C bond *via* Pd-catalyzed *Suzuki* cross-coupling [15] between

Scheme 1



an eletrophilic aromatic synthon and (2,3,4,6-tetramethoxyphenyl)boronic acid (**2**), a synthon that, as far as we know, has not been used in Pd-catalyzed cross-coupling reactions before. The literature reports only reactions involving (methoxyphenyl)-, (dimethoxyphenyl)-, and (trimethoxyphenyl)boronic acids [15a][16]. Therefore, we were interested to study the behavior of 1,2,3,5-tetramethoxybenzene in such cross-coupling reactions to get access to new dimethoxyaryl-substituted benzoquinones.

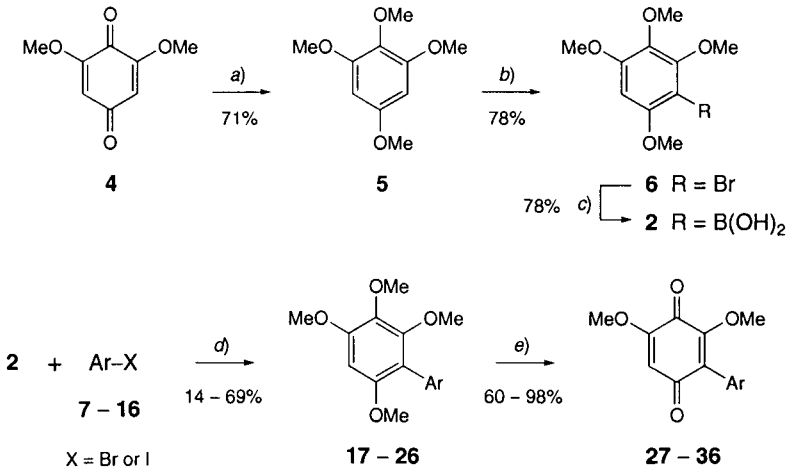
The *Suzuki–Miyaura* Pd-catalyzed cross-coupling between arylboronic acids and aryl halides or aryl triflates has been shown to be a very versatile method for the formation of C–C bonds in both simple and complex biaryls [15]. The group of *Snieckus* developed elegant strategies that combine directed *ortho*- and remote-metalation reactions with *Suzuki–Miyaura* cross-coupling in the synthesis of kinamycins, as well as for a diverse array of other natural products [17]. This transformation enjoys a broad scope and wide functional-group tolerance. However, in reactions involving sterically hindered substrates, limited success has been archieved [18].

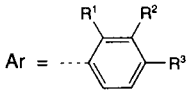
The oxidative demethylation of 1,4-hydroquinone dimethyl ether to afford the corresponding quinone is a well-known reaction [19]. Therefore, we envisaged a retrosynthetic approach towards **1** by oxidation of the corresponding biaryl **3**, as shown in *Scheme 1*. This compound, in turn, could be obtained from the aromatic building block **2** and an aryl or heteroaryl bromide (or idodide) *via* metalation of the latter, followed by cross-coupling.

Herein, we report the use of Pd-catalyzed cross-coupling between aryl bromides (or iodides) and the sterically hindered (2,3,4,6-tetramethoxyphenyl)boronic acid (**2**) to access a variety of highly functionalized aryl and heteroaryl quinones.

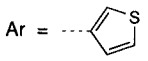
Results and Discussion. – The protection of a 1,4-benzoquinone as the dimethyl ether of its hydroquinone form allows the manipulation of the molecule under strongly anionic conditions. Thus, as shown in *Scheme 2*, 2,6-dimethoxy-1,4-benzoquinone (**4**) was first reductively *O*-methylated [20], leading to 1,2,3,5-tetramethoxybenzene (**5**; 71%). In the presence of *N*-bromosuccinimide (NBS), **5** was converted into the bromo derivative **6** (78%). The latter was metalated under standard conditions (BuLi, TMEDA, THF, –78°) [21], followed by trimethyl-borate quenching and hydrolysis, to afford the crude phenylboronic acid **2** (78%) as a stable and easily handled solid (78%). Compound **2** was then submitted to modified *Suzuki* cross-coupling (DME, aqueous Na_2CO_3, [$Pd(Ph_3P)_4$], reflux) [22] with eight different aryl halides (**7**–**14**) and two heteroaryl halides (**15**, **16**), leading to the biaryl derivatives **17**–**26** in isolated yields of 14–69% (*Table 1*).

Scheme 2

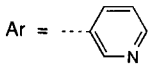




	R^1	R^2	R^3
7, 17, 27	H	H	H
8, 18, 28	H	H	Br
9, 19, 29	H	H	F
10, 20, 30	H	H	NO_2
11, 21, 31	H	H	CHO
12, 22, 32	CN	H	H
13, 23, 33	H	CN	H
14, 24, 34	H	H	CN



15, 25, 35



16, 26, 36

a) 1. 10% $Na_2S_2O_4$, Et_2O, r.t., 1 h; 2. $(MeO)_2SO_2$, 50% KOH, r.t., 3 h. *b*) NBS, $CHCl_3$, r.t., 3 h. *c*) 1. BuLi, TMEDA, THF, −78°, 1 h; 2. $(MeO)_3B$, −78°, 2 h; 3. Hydrolysis. *d*) $[Pd(PPh_3)_4]$, 2M aq. Na_2CO_3, 1,2-dimethoxyethane (DME), reflux, 3 h. e) AgO, 1,4-dioxane, 6M aq. HNO_3, r.t., 30 min.

Boronic acid **2** reacted satisfactorily (73–95% conversion within 3 h) with the aryl halides **7**–**9**, **13** and **14**. However, the cross-coupling with **10** and **11** was retarded, leading to hydrolysis of **2** back to 1,2,3,5-tetramethoxybenzene (**5**). The coupling with the heteroaromatic substrate **15** was extremely slow, resulting in catalyst decomposition (precipitation of Pd-black) and low conversion. Longer reaction times did not increase the yield of the desired biaryl significantly, but rather resulted in increased amounts of the hydrolytic deboration product **5**. The coupling reaction with 2-bromobenzonitrile (**12**) led mainly to the unsymmetrical product, but the conversion and the yield remained low.

Table 1. *Synthesis of the Biaryls* **17**–**26** via *Pd⁰-Catalyzed Cross-Coupling between* **2** *and the Haloarenes* **7**–**16**. Conditions: 3 mol-% [$Pd(PPh_3)_4$], 0.8 mmol of **2**, 0.6 mmol of haloarene, 2 mmol aq. 2N Na_2CO_3 soln., 1,2-dimethoxyethane (DME), reflux. For details and structures, see the *Exper. Part* and *Scheme 2*.

Substrate	Reaction time [h]	Conversion [%][a])	Product[b])	Yield [%][c])	M.p. [°]
7	3	79	**17**	79 (63)	89.7–91.9 [d])
8	3	84	**18**	76 (58)	109.2–110.8
9	3	73	**19**	68 (42)	88.6–90.2
10	3	59	**20**	46 (27)	103.2–105.1
11	3	40	**21**	40 (34)	130.2–132.0
12	4	32	**22**	32 (14)	133.0–134.0
13	3	90	**23**	90 (66)	79.0–81.0
14	3	95	**24**	95 (69)	122.0–123.0
15	4	53	**25**	49 (36)	93.2–95.4
16	2	47	**26**	49 (43)	112.4–114.8

[a]) Percent conversion determined by GC analysis of the crude products. [b]) All products were recrystallized from hexane/$CHCl_3$. [c]) Extrapolated to percent conversion (by GC); in parentheses, the isolated yields are given. [d]) Lit. value: 92° [32].

The presence of both electron-withdrawing and electron-attracting groups can, in some cases, accelerate protonolysis [18][23], which, together with steric hindrance, might explain the low yields of conversion. Sterically hindered arylboronic acids usually give rise to low coupling yields, and the hydrolytic deboronation by C–B bond cleavage predominates [18][24]. *Suzuki* and others have demonstrated that the cross-coupling of sterically hindered boronic acids with haloarenes is greatly enhanced by the use of stronger bases such as $Ba(OH)_2$, NaOH, K_3PO_4 and TlOH [23a][25]. In our work, the use of a saturated aqueous solution of $Ba(OH)_2$ and K_3PO_4 instead of the 2M solution of Na_2CO_3 had little effect on the outcome of the coupling between **2** and **12**, but gave rise to lower yields of **22** (17 *vs.* 26%, respectively). To improve the yield, an alternative approach could be to convert the boronic acid to a boronic acid ester [18d], or to exchange [$Pd(Ph_3P)_4$] with [$Pd_2(dba)_3$] [26].

Cleavage of Me ethers used for 1,4-benzoquinone protection is most commonly performed by exposure to argentic oxide or ammonium cerium nitrate [19]. However, with an organic oxidant such as Ce^{IV}, side reactions (oxidative dimerization) frequently prevail [19]. Despite the high prize of AgO, this reagent was used (since readily available in our laboatory). Thus, compounds **17**–**26** were oxidatively demethylated [19b] with AgO to afford the (methoxyaryl)-substituted 1,4-benzoquinones **27**–**36** in yields of 70–98%, and with high cleavage selectivity (*Table 2*). Oxidative side reactions were shown to be negligible, and, because of the instability of 1,2-benzoquinones, isolation of further side products was not attempted. The oxidative demethylation of **17**–**26** was, in fact, favored by the presence of the additional MeO groups. The orientation of substituents was, thus, of lesser importance, and the 2,6-disubstitution facilitated the formation of the 1,4-benzoquinone nucleus.

Conclusions. – Pd-Catalyzed cross-coupling of (2,3,4,6-tetramethoxyphenyl)boronic acid (**2**) with a variety of aryl or heteroyryl halides, followed by oxidative deprotection, provides a strategy towards functionalized 2-aryl or 2-heteroaryl-1,4-

Table 2. *Synthesis of the 1,4-Benzoquinones* **27**–**36** via *Oxidative Demethylation of the Biaryls* **17**–**26**. Conditions: AgO, HNO_3, 1,4-dioxane, r.t., 30 min (for details and structures, see the *Exper. Part* and *Scheme 2*).

Substrate	Product[a])	Isolated yield [%]	M.p. [°]
17	**27**	72	109.4–110.6[b])
18	**28**	96	189.7–192.5
19	**29**	98	180.7–182.6
20	**30**	72	227.0–229.0
21	**31**	70	191.0–192.0
22	**32**	60	gum[c])
23	**33**	67	205.0–207.0
24	**34**	70	227.0–230.0
25	**35**	72	106.2 - 107.8
26	**36**	96	160.2 - 162.9

[a]) All products were recrystallized from hexane/$CHCl_3$ (except for **22**). [b]) Lit. value: 110° [32]. [c]) Anal. calc. for $C_{15}H_{11}NO_4$: C 66.91, H 4.12, N 5.20; found: C 66.96, H 4.21, N 5.36.

benzoquinones with MeO groups in 3- and 5-position. Moderate to excellent yields of the diaryls can be obtained, and a variety of functional groups (Br, F, NO_2, CHO, CN) on the aryl ring are tolerated. The yield of the Pd-catalyzed reaction appears to be very sensitive to *ortho*-substitution of the aryl group of the boronic acid moiety.

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Experimental Part

General. All reactions involving O_2- and/or H_2O-sensitive reagents were carried out under N_2 atmosphere in oven-dried glassware. Low temperatures (*ca.* −78°) were generated by an acetone/liquid-N_2 bath. Anh. solvents (Et_2O, THF, 1,2-dimethoxyethane (DME), CH_2Cl_2, DMSO) were purified and dried according to standard procedures [27]. BuLi (hexane soln.) was purchased from *Fluka* and periodically titrated against 2,5-dimethoxybenzylalcohol [28]. TMEDA (*N,N, N′,N′*-tetramethylethylenediamine) was purchased from *Aldrich*, stored over CaH_2, and distilled over CaH_2 before use. The aryl halides **7**–**16** were commercially available. 2,6-Dimethoxy-1,4-benzoquinone (**4**) was prepared from wood tar fractions according to [29]. The catalyst [$Pd(Ph_3P)_4$] was prepared by hydrazine reduction of $PdCl_2$ [30] and stored under N_2 at −10°. Flash chromatography (FC) was carried out on silica gel (230–400 mesh). Compounds **5** and **6** were identified by spectral comparison with authentic samples [31][32]. M.p.: *Mettler FP-90* apparatus; uncorrected. IR Spectra: *Shimadzu IR-408* instrument, KBr pellets; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker Avance DRX-400* instrument (400 and 100 MHz, resp.); in $CDCl_3$; chemical shifts δ in ppm rel. to Me_4Si (= 0 ppm) as internal standard; single-bond heteronuclear $^1H/^{13}C$ connectivities were determined by 2D ^1H-detected HMQC experiments, and two- and three-bond $^1H/^{13}C$ connectivities were determined by 2D ^1H-detected HMBC experiments. Elemental analyses: *Perkin-Elmer PE-2400 CHN* instrument.

(2,3,4,6-Tetramethoxyphenyl)boronic Acid (**2**). BuLi (1.8 mmol; 1.6M in hexane) was slowly added to a cold (−78°) soln. of *2-bromo-1,3,4,5-tetramethoxybenzene* (**6**) (250 mg, 0.9 mmol) and TMEDA (179 mg, 1.8 mmol) in anh. THF (4 ml). The resulting soln. was stirred for 1 h at −15°, cooled to −78°, and then treated with $(MeO)_3B$ (370 mg, 3.6 mmol). This mixture was allowed to reach r.t. over 3 h. The reaction was then quenched with sat. aq. NH_4Cl soln. (4 ml). The mixture was acidified with aq. 10% HCl to pH 4–6, and extracted with $CHCl_3$. The combined org. layers were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure to afford a yellow oil. The latter was crystallized at −10° from Et_2O/hexane: 170 mg (78%) of **2**. Crystalline white solid. M.p. 84–85°. IR (KBr): 3500 (br., OH). ^1H-NMR (400 MHz, $CDCl_3$): 3.79 (*s*, MeO); 3.84 (*s*, MeO); 3.91 (*s*, MeO); 3.98 (*s*, MeO); 6.33 (*s*, H–C(5)); 7.15 (br. *s*, 2 OH, exchangeable with D_2O). ^{13}C-NMR (100 MHz, $CDCl_3$): 55.52; 56.09; 60.96; 61.84; 91.84; 132.27; 153.75; 156.24; 159.50; 161.10. Anal. calc. for $C_{10}H_{15}BO_6$: C 49.62; H 6.25; found: C 49.82, H 6.41.

General Procedure for the Cross-Coupling of **2** *with the Haloarenes* **7**–**16**. A three-neck flask, equipped with a reflux condenser, septum, and stirring bar, was filled with the halide (0.6 mmol) and [Pd(Ph_3P)$_4$] (3 mol-%) in DME (10 ml) under N_2 atmosphere. The mixture was stirred for 10 min at 50°. To this soln. was added **2** (0.8 mmol), dissolved in a minimum amount of EtOH/DME 1:2, followed by aq. Na_2CO_3 (4 ml of a 2M soln.). This mixture was refluxed under stirring. At suitable time intervals, an anal. sample was submitted to GC analysis. After 3 h, the flask was cooled to r.t., and the mixture was treated with sat. aq. NH_4Cl soln. (4 ml) and extracted with $CHCl_3$. The org. layer was washed with brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resulting crude product was purified by FC (SiO_2; hexane/AcOEt 9:1) to afford the corresponding biaryl. All products (**17**–**26**, resp.) were fully characterized by IR, and ^{1}H- and ^{13}C-NMR, as well as by elemental analyses (CHN) [33]; the yields and m.p. are listed in *Table 1*.

General Procedure for the Oxidative Demethylation of the Biaryl Compounds **17**–**26**. HNO_3 (0.1 ml of a 6M soln.) was added to a mixture of the biaryl compound (0.2 mmol), AgO (0.10 g, 0.8 mmol), and 1,4-dioxane (4 ml; redistilled from Na). The mixture was stirred at r.t. for 30 min. Then, the reaction was terminated by addition of a mixture of $CHCl_3/H_2O$ 4:1 (10 ml). The mixture was extracted with H_2O (2 ml), the $CHCl_3$ layer was dried (Na_2SO_4) and evaporated under reduced pressure, and the resulting crude product was purified either by FC (SiO_2) or recrystallization. All compounds were fully characterized by IR, ^{1}H- and ^{13}C-NMR, as well as elemental analyses (CHN) [33]; the yields and m.p. of the products (**27**–**36**) are listed in *Table 2*.

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