Abstract: The preparation of biaryls via oxidation of organocuprates with easily synthesized octahydro[1,4:5,8]dimethanoanthraquinone (DAQ) is described. The oxidative coupling of organocuprates using DAQ was successfully employed for the preparation of highly hindered biaryls and 9- and 10-membered macrocycles containing biaryl linkages. The oxidative reactivity of DAQ towards organocuprates is found to be similar to the commonly utilized quinones such as duroquinone (DQ) and tetra-tert-butylibiphenoxoquinone (BQ) and is in accord with their similar reduction potentials (measured by an electrochemical method). The structures of the quinones are also established with the aid of X-ray crystallography. The usage of DAQ for biaryl synthesis is advocated owing to the ready separation of reduced DAQ-H2 from biaryls as well as its ready-availability in multi-gram quantities.

Key words: quinones, one-electron transfer, organocuprates, biaryls, macrocycles

Aryl–aryl bond-forming reactions are of significant importance not only as tools in modern organic syntheses of natural products, but also for the preparation of novel materials used in the emerging areas of molecular electronics and nanotechnology. Generally, the construction of biaryl linkages is carried out from various aryl halides using palladium, nickel, copper, and iron-catalyzed chemistry.

Recently, a number of reports have shown that the formation of biaryl linkages can also be accomplished via electron-transfer oxidation of organomagnesium and lithium reagents, or organocuprates using mild oxidants such as tetramethyl-p-benzoquinone (or duroquinone, DQ), tetra-tert-butylibiphenoxoquinone (BQ), substituted nitrobenzenes, etc. These synthetic transformations for the formation of biaryl linkages are important owing to the fact that they allow the construction of macrocycles containing biaryl linkages.

Our interest in the preparation of a homologous series of macrocycles containing tetramethoxybiaryl moieties prompted us to explore the usage of this transformation using the readily-available and cheap octahydro[1,4:5,8]dimethanoanthraquinone (hereafter referred to as dimethanoanthraquinone or DAQ), which has largely escaped attention as an oxidant. Herein, we advance the usage of DAQ as an oxidant for the formation of biaryl linkages due to the following reasons. Firstly, the precursor to DAQ (hydroquinone) can be easily obtained in multi-gram quantities (25–100 g) using readily available and cheap starting materials from a recently published procedure in Organic Syntheses (Scheme 1).

Thus, a reaction of cyclopentadiene with p-benzoquinone affords a quantitative yield of the Diels–Alder adduct 1, which is easily hydrogenated to the corresponding diol 2 in quantitative yield. The treatment of diketone 2 with one equivalent of bromine in chloroform or dichloromethane gives a quantitative yield of the sparingly soluble hydroquinone 3. Secondly, the resulting hydroquinone 3 (without isolation) can be efficiently oxidized to the corresponding quinone (DAQ) using a catalytic amount of nitrogen oxides (which can be easily generated using sodium nitrite and sulfuric acid) and air or oxygen as the oxidant. A detailed, one-pot procedure for a convenient preparation of DAQ from 2 is described in the experimental section. It is also noted that DAQ is readily soluble in various organic solvents; however the corresponding hydroquinone, DAQ-H2 (3), is almost insoluble in various organic solvents, which allows the ready separation of the biaryls from the reduced hydroquinone. It is noteworthy that both tetra-tert-butylibiphenoxoquinone (BQ) and reduced BQ-H2 are equally soluble in various organic solvents owing to the presence of bulky tert-butyl...
groups (vide infra), which prevent hydrogen bonding interactions amongst the phenolic OH groups and thereby complicating a ready isolation of the biaryls from the reaction mixtures. Finally, the unhindered duroquinone (DQ) is expected to undergo association with reduced DQ leading to the formation of a dimer anion radical and quinhydrone, and thus necessitates the usage of excess quinone for the coupling reactions.5

Accordingly, herein we demonstrate using a variety of examples, that all the three quinones (DQ, BQ, and DAQ) serve as effective oxidants for the preparation of biaryls from arylcuprates. The usage of DAQ for biaryl synthesis is advocated because of its ready availability in multi-gram quantities as well as the advantages presented above. Moreover, we show that the biaryl synthesis presented herein can be employed for the preparation of hitherto unknown large macrocycles containing biaryl linkages as follows.

We initially compared the efficacy of DAQ with commonly utilized DQ5 and BQ6 for the oxidative coupling of an arylcuprate derived from 2-bromoanisole. Thus, a lithiation of 2-bromoanisole with n-BuLi in diethyl ether at −78 °C (1 h) followed by transmetalation using 0.5 equiv of CuCN produces a diarylcuprate, which was subjected to oxidative coupling using DAQ, DQ, and BQ in three separate experiments to afford 2,2′-dimethoxybi-phenyl, which, in each case, was formed in excellent yield (Equation 1).

![Equation 1](image1)

The oxidative coupling using DAQ is not limited to the organocuprates derived from organolithiums, but can also be carried out equally effectively when they are derived from the corresponding Grignard reagents (Equation 2).

![Equation 2](image2)

The efficacy of the usage of DAQ for the oxidation of organocuprates was further demonstrated using a variety of examples (Table 1). The procedure in Equation 1 can be employed equally effectively for the preparation of sterically hindered biaryls (Table 1, entries 4–6). It is noted that the highly hindered biaryl 8 was produced in a relatively low yield (25%), however, in this context, it is also important to note that attempted preparation of 8 via Kumada coupling12 did not afford the desired biaryl 8, even in trace quantity!

The structures of various biaryls in Table 1 were established by 1H/13C NMR spectroscopy and were further confirmed either by mass spectrometry (see experimental section) or by comparison with the authentic samples.13

The versatility of the procedure in Equation 1 was further demonstrated by its application for the preparation of macrocycles with 9- and 10-membered rings containing a tetramethoxybiaryl linkage.8 It has been reported that compounds 11a–c containing smaller ring (i.e., 6, 7, and 8-membered rings) linkage between the tetramethoxybiaryls can be readily synthesized via oxidative coupling of the a,ω-bis(3,4-dimethoxyphenyl)alkanes 10a–c using various chemical oxidants14 or via electrochemical oxidation15 (Equation 3).

![Equation 3](image3)

However, attempted preparation of the 9- and 10-membered macrocycles 11d and 11e via oxidative cyclization of 10d16 and 10e17 according to the procedure in Equation 3, yielded only a complex mixture of products; and the mass spectral analysis of the soluble components of these mixtures did not show the presence of 11d and 11e (Scheme 2).
However, bromination of 10d (or 10e) with bromine in dichloromethane easily afforded the corresponding dibromo derivative 12d (or 12e) in quantitative yield. A double lithiation of 12d (or 12e) with n-BuLi (2.2 equiv) in diethyl ether at –78 °C (1.5 h) followed by transmetalation using 1 equivalent of CuCN and the oxidative coupling using DAQ afforded, after chromatographic purification, macrocycle 11d (or 11e), albeit in somewhat low yield (20–26%) (Scheme 2).

In order to gain further insight into the oxidative reactivity of various quinones towards organocuprates, their electrochemical reduction potentials were determined by cyclic voltammetry as follows. Each quinone was subjected to an electrochemical reduction at a platinum electrode as a 2 mM solution in anhydrous tetrahydrofuran containing 0.1 M Bu₄NPF₆ as the supporting electrolyte. The cyclic voltammograms are compiled in Figure 1. The p-benzoquinone derivatives, DAQ and DQ, showed only one reversible reduction wave (see blue curves in Figure 1) corresponding to the formation of the monoanion radical at reduction potentials of –0.81 and –0.98 V versus SCE, respectively. The second reduction wave was found to be irreversible for both DAQ and DQ, and occurring at relatively negative potentials (see gray curves in Figure 1). On the other hand, BQ showed two reversible reduction waves corresponding to the formation of the anion radical (E_{red1} = –0.66 V vs. SCE) and dianion (E_{red2} = –1.18 V vs. SCE), respectively. The first reduction potentials of the three quinones differed only by ~0.3 V; however, the potentials of the quinones employed herein were sufficiently high to promote the highly exergonic one-electron transfer from the electron-rich diarylcuprates (E_{ox} ~ –2 V vs. SCE).¹⁸

The structures of DAQ as well as BQ and DQ were also determined at –173 °C by X-ray crystallography¹⁹ and are compared in Figure 2. The C=O bond lengths in the various quinones were, expectedly, found to be rather invariant (1.227, 1.226, and 1.228 Å for DAQ, DQ, and BQ, respectively), and the limited changes in C=O bond lengths were in line with the observed C=O stretching frequencies (1644, 1636, 1605 cm⁻¹ for DAQ, DQ, and BQ, respectively) in their infrared spectra, recorded as KBr pellets.

### Table 1 Various Biaryls Synthesized

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Method¹</th>
<th>Yield (%)</th>
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<td><img src="image2" alt="Image" /></td>
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<td><img src="image14" alt="Image" /></td>
<td>Method A</td>
<td></td>
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</tbody>
</table>

¹ Method A: using organolithiums; Method B: using Grignard reagents.

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In summary, we have demonstrated that the easily synthesized octahydro[1,4:5,8]dimethanoanthraquinone (DAQ) can be successfully utilized as an efficient oxidant for the biaryl synthesis using organocuprates. The efficacy of the procedure is further delineated by the preparation of a number of highly hindered biaryls as well as 9- and 10-membered macrocycles containing biaryl linkages. It is believed that the ready availability of DAQ as well as the ease of the separation of biaryls from the reaction mixtures will lead to its widespread application in biaryl syntheses.

Melting points are uncorrected. IR spectra were recorded using KBr disks on a Nicolet 560 Magna infrared spectrometer. NMR spectra were obtained on a Varian NMR spectrometer (300 MHz) as CDCl₃ solutions using TMS as an internal standard reference. GC-MS spectra were obtained on a Fisons 8000 Trio instrument at an ionization potential of 70 eV. TLC experiments were carried out on precoated silica gel plates (hexanes–EtOAc, 5:1). Solvents and reagents were purchased from commercial sources. 2-Bromoanisole, 4-bromoanisole, bromobenzene, and 2-bromo-4,4¢-di-tert-butylbiphenyl,13 2-tert-butyl-4,5-dimethoxybromobenzene,20 a,ω-bis(dimethoxyphenyl)alkanes 10d16 and 10e17 were prepared according to the literature procedures.

Figure 1 Comparison of the cyclic voltammograms of various quinones (2 mM) in THF (0.1 M Bu₄NPF₆) at a scan rate of 200 mV s⁻¹. Note that the first reduction wave of both DAQ and DQ are completely reversible (blue curves) if scanning is terminated before the start of the second reduction event.

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Bromination of 4,4¢-Bis(3,4-dimethoxyphenyl)alkanes 10d and 10e; 1,5-Bis(6-bromo-3,4-dimethoxyphenyl)pentane (12d);

**Typical Procedure**

To a solution of 1,5-bis(3,4-dimethoxyphenyl)pentane (10d; 2.0 g, 5.8 mmol) in CH₂Cl₂ (50 mL) was added dropwise a solution of Br₂ (2.1 g, 12.8 mmol) in CH₂Cl₂ (20 mL). The resulting mixture was stirred for 30 min and the reaction was quenched by the addition of 10% aq NaHSO₄ (50 mL). The organic layer was separated and washed further with aq NaHSO₄ (2 × 25 mL) and dried (MgSO₄). Evaporation of the solvent afforded 12d as a white solid; yield: 2.8 g (95%); colorless crystals; mp 77–79 °C.

1 H NMR (CDCl₃, 400 MHz): δ = 1.62 (m, 4 H), 1.59 (m, 4 H), 3.34 (s, 6 H), 5.60 (s, 2 H), 6.70 (s, 2 H), 6.71 (s, 2 H), 6.98 (s, 2 H).

13C NMR (CDCl₃, 100 MHz): δ = 112.32, 133.98, 134.51, 146.75, 148.40.

**MS (70 eV): m/z:** 516 [M⁺].

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**X-ray Crystal Structure Analyses of DAQ, BQ, and DQ**

All diffraction intensity data were collected with a Bruker Smart Apex CCD diffractometer at 173(2) K using Cu-radiation (1.54178 Å). All structures were solved using direct methods, completed by difference Fourier syntheses, and refined by full matrix least-squares procedures. Crystallographic data, details for data collection, and refinement methods for each structure are summarized below.

**DAQ**

Yellow crystals of DAQ were grown from a 1:9 mixture of EtOAc–hexanes. A yellow-colored crystal with dimensions (0.12 × 0.12 × 0.08 mm³) was selected for data collection. Empirical formula C₉₆H₁₂O₂; Formula weight 240.29; Crystal system = triclinic; Space group P½; Z = 4; Unit cell dimensions a = 6.08580(10) Å, b = 12.1696(3) Å, c = 16.5007(4) Å; \( a = 106.9130(10)°, \) \( \beta = 94.3603(10)°, \) \( \gamma = 90.2330(10)°; \) \( V = 1165.38(4) Å³; \) D (calculated) = 1.370 g cm⁻³; m = 0.706 mm⁻³. The total number of reflections measured was 14333, of which 3856 re-

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**PAPER**

Biaryl 4–9; General and Typical Procedures

**Method A, General Procedure:** An argon-flushed Schlenk flask (100 mL), equipped with a magnetic stirrer and a rubber septum was charged with the respective aryl bromide (2.5 mmol) in anhyd Et₂O (50 mL). The mixture was cooled to –78 °C and n-BuLi (1.1 mL, 2.75 mmol, 2.5 M in hexane) was added dropwise. After stirring for 1.5 h at –78 °C, CuCN (112 mg, 1.25 mmol) was added to the mixture and it was vigorously stirred at r.t. until the CuCN had dissolved (~30 min). Solid DAQ (0.7 g, 3 mmol) was added to this stirred solution and the resulting mixture was stirred for an additional 4 h. At which time, the reaction was quenched by the addition of 2 N aq HCl (~25 mL) of the crude mixture with Zn dust (~1 g) in the presence of AcOH (1 mL) until the yellow color of DAQ had completely disappeared (~5 min). The resulting mixture was filtered to separate Zn dust and DAQ-H₂ (Note 2), and the filtrate was washed with 10% aq NaHCO₃ (~25 mL) and the aqueous layer was further extracted with CH₂Cl₂ (3 × 20 mL). The combined organic extracts were dried (MgSO₄) and concentrated under reduced pressure. Any unreacted DAQ was converted into DAQ-H₂ by heating a CH₃Cl₂ solution (~25 mL) of the crude mixture with Zn dust (1 g) in the presence of AcOH (1 mL) until the yellow color of DAQ had completely disappeared (~5 min). The resulting mixture was filtered to separate Zn dust and DAQ-H₂ (Note 2), and the filtrate was washed with 10% aq NaHCO₃ (~25 mL), dried (MgSO₄), evaporated, and purified by column chromatography on silica gel using a 9:1 mixture of hexanes–EtOAc as eluent.

1H NMR (CDCl₃): δ = 1.58 (m, 2 H), 2.46 (m, 2 H), 3.80 (s, 6 H), 3.90 (s, 6 H), 6.54 (s, 2 H), 6.98 (s, 2 H).

13C NMR (CDCl₃): δ = 220.97, 28.36, 29.16, 56.06, 56.11, 111.13, 111.33, 132.87, 134.85, 146.37, 148.53.

MS (70 eV): m/z = 342 [M⁺].

6,7,8,9-Tetrahydro-2,3,11,12-tetramethoxydibenzo[a,c]cyclo-

11d)

Yield: 20%; colorless, low-melting solid.

1H NMR (CDCl₃, 400 MHz): δ = 1.72 (m, 4 H), 2.06 (m, 2 H), 2.52 (m, 4 H), 3.84 (s, 6 H), 3.91 (s, 6 H), 6.66 (s, 2 H), 6.72 (s, 2 H).

13C NMR (CDCl₃, 100 MHz): δ = 28.58, 29.47, 33.24, 56.15, 56.17, 111.81, 112.32, 133.98, 134.51, 146.75, 148.40.

MS (70 eV): m/z = 356 [M⁺].

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**Synthesis** 2008, No. 23, 3769–3774 © Thieme Stuttgart · New York
reflections were symmetrically nonequivalent. Final residuals were
R1 = 0.0424 and wR2 = 0.0604 for 3856 reflections with I > 2σ(I).

BQ
Yellow crystals of BQ were grown from a mixture of CH2Cl2–aceto-
tone. A yellow-colored crystal with dimensions (0.60 × 0.25 × 0.15
mm3) was selected for data collection. Empirical formula C2,H10O2;
Formula weight 164.20; Crystal system = triclinic; Space group
P̅T; Z = 1; Unit cell dimensions a = 6.02230(10) Å, b = 10.2933(2)
Å, c = 10.3749(2) Å; a = 81.3820(10)°, β = 109.368(4)°, γ = 109.057(4)°,
m = 0.514 mm–1. The total number of reflections measured was
5087, of which 2046 reflections were symmetrically nonequivalent.
Final residuals were R1 = 0.0348 and wR2 = 0.0361 for 2046 re-
fections with I > 2σ(I).

DQ
Yellow crystals of DQ were grown from a mixture of CH2Cl2–
MeOH. A yellow-colored crystal with dimensions (0.40 × 0.08 × 0.08
mm3) was selected for data collection. Empirical formula C28H40O2;
Formula weight 422.07(7); Unit cell dimensions a = 8.6795(8) Å,
b = 9.0471(8) Å; a = 109.368(4)°, β = 109.368(4)°, γ = 103.303(4)°;
V = 613.64(2) Å3; D (calculated) = 1.106 g cm–3; Crystal system = tri-
clinic; Space group P̅T; Z = 2; Unit cell dimensions
a = 10.3749(2) Å, b = 10.2933(2) Å, c = 10.3749(2) Å; a = 81.3820(10)°,
β = 109.368(4)°, γ = 109.057(4)°, m = 0.514 mm–1. The total number of reflections measured was
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Final residuals were R1 = 0.0348 and wR2 = 0.0361 for 2046 re-
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Cambridge Crystallographic Data Centre as supplementary
publication numbers CCDC-701965, 701966, and 701967.
Copies of the data can be obtained free of charge on applic-
ation to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK
[E-mail: deposit@ccdc.cam.ac.uk; Fax: +44(1223)336033
or via www.ccdc.cam.ac.uk/conts/retrieving.html].