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A Streamlined Synthesis of 2,3-Dihydrobenzofurans *via* the *ortho*-Quinone Methides Generated from 2-Alkyl-Substituted Phenols

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Abstract: A facile method for the stereoselective synthesis of *trans*-2,3-dihydrobenzofurans from *ortho*-quinone methides *in situ* generated from readily available 2-alkyl-substituted phenols using silver oxide-mediated oxidation has been developed. Additionally, the 2,3-dihydrobenzofurans can be further transformed into the aromatized 2,3-disubstituted benzofurans in the presence of DDQ.

Keywords: 2,3-dihydrobenzofurans; *ortho*-quinone methides; synthesis

2,3-Dihydrobenzofuran derivatives are an important class of compounds due to their remarkable significance in various biological active molecules, synthetic drugs and natural products.[1] For instance, (+)-conocarpan which was first isolated from the wood of *Conocarpus erectus*[2] acts as an insecticidal,[1a] antifungal[1b] and antitrypanosomal agent.[1c] Obtusafuran is a quinone reductase[1d] and propafenone-derived dihydrobenzofurans possess anti-multidrug resistance properties[1e] (Figure 1). Additionally, 2,3-dihydrobenzofurans have also been developed for the treatment of traumatic and ischemic central nervous system injury.[3] Thus, the synthesis of 2,3-dihydrobenzofurans has received extensive attention in the past decades and various efficient methodologies for the construction of 2,3-dihydrobenzofurans have been developed, including electrocyclization,[4] radical cyclization,[5] anionic cyclization,[6] transition metal-catalyzed cyclization,[7] cycloaddition,[8] biomimetic coupling,[9] Lewis acid-promoted reactions.[10] Although significant progress has been made in the synthesis of 2,3-dihydrobenzofurans, most of these existing routes have several drawbacks involving poor chemo- and/or diastereoselectivities, unsatisfactory yields, tedious processes and harsh reaction conditions, prohibiting their wider application. Therefore, the development of a convenient, efficient and atom-economical method for the rapid synthesis of these derivatives is still highly desirable.

ortho-Quinone methides (*o*-QMs) are emerging as versatile intermediates in a large number of chemical and biological processes.[11] Consequently, several approaches have been successfully developed for generating *o*-QMs, including tautomerization, oxidation, acid or base catalysis, thermolysis, photolysis and olefination of *o*-quinones which have been described in the literature.[12,13] Recently, we reported an efficient approach for the generation of *o*-QMs intermediates under the mild basic conditions which further underwent reaction with sulfur ylides to afford the *trans*-2,3-dihydrobenzofurans with high yields (Scheme 1).[14a] Considering that the *o*-QMs intermediates could be conveniently generated by the oxidation of easily available 2-alkyl-substituted phenol derivatives,[13a–c,15] we speculated that the generated *o*-QMs intermediates could be rapidly trapped by sulfur ylides to allow the construction of 2,3-dihydrobenzo-

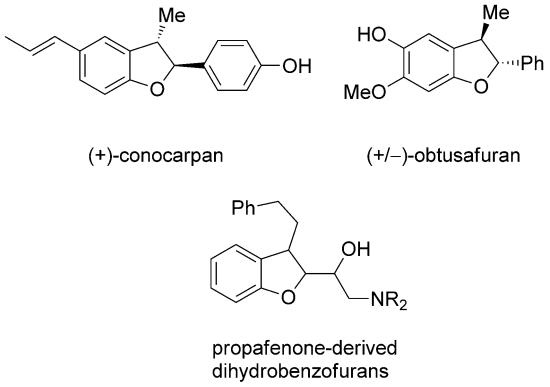
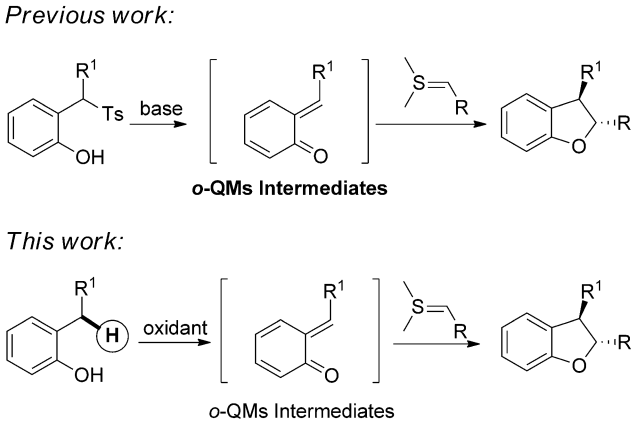


Figure 1. Bioactive 2,3-dihydrobenzofuran derivatives.



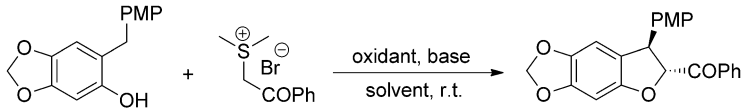
Scheme 1. The new strategy for the synthesis of 2,3-dihydrobenzofurans.

furans, which is more atom-economical and simple in comparison to our previous work. Herein, we disclose a straightforward and atom-economical method for the rapid synthesis of 2,3-dihydrobenzofurans *via* the *o*-QMs generated from 2-alkyl-substituted phenols in the presence of an oxidant (Scheme 1).

Our initial investigation was conducted with 2-alkyl-substituted phenol **1a** (1.2 equiv) and sulfonium salt **2a** as model substrates at room temperature. The oxidant played a crucial role in the reaction and triggered the generation of *o*-QMs intermediates, therefore the oxidant was firstly thoroughly evaluated.

To our delight, the reaction proceeded smoothly to provide the desired product **3a** in 92% yield and excellent an diastereomeric ratio when Ag_2CO_3 was employed as oxidant (entry 1, Table 1). However, the other oxidants, $AgNO_3$, DDQ, BPO and $PhI(OAc)_2$, displayed lower reactivity (entries 2–5) and $K_3[Fe(CN)_6]$ gave only moderate yields albeit with perfect diastereoslectivity (entry 6). Additionally, good yields and diastereoslectivity were also obtained in the presence of Ag_2O as oxidant (entry 7). Subsequently, different solvents were extensively examined, and it was found that the solvent effect displayed a significant influence on the reactivity (entries 8–12). CH_2Cl_2 was proven to be the most favorable solvent with respect to excellent yields and diastereoselectivity. Finally, the influence of base was explored. Several common anionic bases, such as Na_2CO_3, NaOH, KO-*t*-Bu and K_2CO_3, all afforded the desired product in satisfactory yields (entries 12–17). For the reason that K_2CO_3 is cheaper and easy to handle it was chosen as the best base.

Table 1. Optimization for the reaction of 2-alkyl-substituted phenol **1a** with sulfonium salt **2a**.[a]



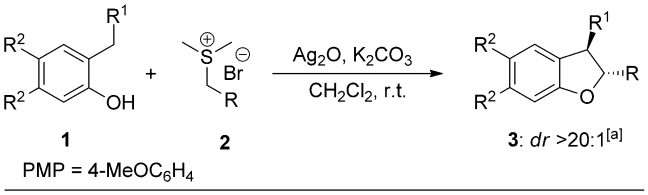
1a **2a** **3a**: *dr* >20:1

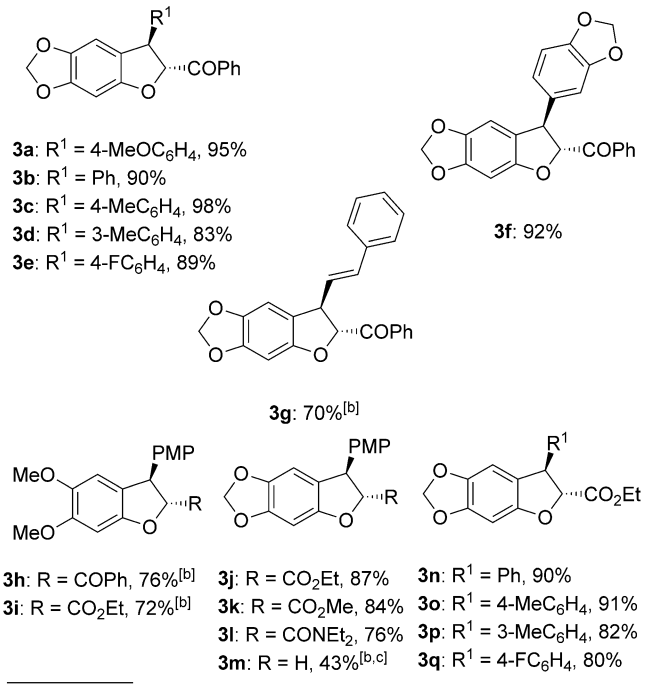
PMP = 4-$MeOC_6H_4$

Entry	Solvent	Base	Oxidant	Yield [%][b]
1	CH_2Cl_2	Cs_2CO_3	Ag_2CO_3	92
2	CH_2Cl_2	Cs_2CO_3	$AgNO_3$	36
3	CH_2Cl_2	Cs_2CO_3	DDQ	31
4	CH_2Cl_2	Cs_2CO_3	BPO	20
5	CH_2Cl_2	Cs_2CO_3	$PhI(OAc)_2$	39
6	CH_2Cl_2	Cs_2CO_3	$K_3[Fe(CN)_6]$	75
7	CH_2Cl_2	Cs_2CO_3	Ag_2O	92
8	Et_2O	Cs_2CO_3	Ag_2O	55
9	THF	Cs_2CO_3	Ag_2O	71
10	toluene	Cs_2CO_3	Ag_2O	45
11	DMF	Cs_2CO_3	Ag_2O	11
12	EtOH	Cs_2CO_3	Ag_2O	87
13	CH_2Cl_2	Na_2CO_3	Ag_2O	89
14	CH_2Cl_2	NaOH	Ag_2O	91
15	CH_2Cl_2	K_3PO_4	Ag_2O	88
16	CH_2Cl_2	KO-*t*-Bu	Ag_2O	97
17	CH_2Cl_2	K_2CO_3	Ag_2O	95

[a] *Reaction conditions:* **1a** (0.24 mmol), **2a** (0.20 mmol), base (1.2 equiv.), oxidant (2.0 equiv.), solvent (3 mL), room temperature, 12 h. DDQ = 2,3-dichloro-5,6-dicyanobenzoquinone; BPO = benzoyl peroxide.

[b] Isolated yields.





[a] *Reaction conditions:* **1** (0.24 mmol), **2** (0.20 mmol), K_2CO_3 (1.2 equiv.), Ag_2O (2.0 equiv.), CH_2Cl_2 (3 mL), room temperature, 12 h. Isolated yields and all of the *dr* >20:1.
[b] KO-*t*-Bu (1.2 equiv.).
[c] Trimethylsulfoxonium iodide was used instead of sulfonium salts.

Scheme 2. Scope of the reaction of 2-alkyl-substituted phenols **1** with sulfonium salts **2**.

With the aforementioned reaction conditions in hand, we explored the reaction scope using a variety of 2-alkyl-substituted phenols **1** and sulfonium salts **2**[16] (Scheme 2). In general, the transformations performed very well and moderate to excellent yields were obtained. Notably, for aryl substituents R^1, the electronic property had little influence on the yield and diastereoselectivity. For example, the reactions furnished the desired product **3a** and **3e** in the 95% and 89% yield, respectively. Interestingly, vinyl substrate **1g** was a suitable reaction partner and provided the product in the good yield which could then be applied to further transformations. Nevertheless, replacement of substrate **1a** by 4,5-dimethoxy-2-(4-methoxybenzyl)phenol resulted in a decrease of yield. Futhermore, with a series of sulfur ylides the reactions proceeded smoothly, and moderate to good yields as well as excellent diastereoselectivities were observed. Moreover, the unstable sulfur ylide trimethylsulfoxonium iodide could react with **1a** to deliver the desired 2,3-dihydrobenofuran product (**3m**) in moderate yield when KO-*t*-Bu was employed, possibly owing to the fact that the strong base KO-*t*-Bu accelerated the rate of the reaction and inhibited the dimerization or polymerization of *o*-QMs.

R^1	4-$MeOC_6H_4$	Ph
yield [%]	80 (**4a**)	67 (**4b**)

Scheme 3. Synthesis of aromatic 2,3-disubstituted benzofurans **4**.

The structure and stereochemistry of **3** were determined by the combination of NMR, HR-mass spectroscopy and single-crystal X-ray diffraction analysis {for the structure of *trans-N,N*-diethyl-7-(4-methoxyphenyl)-6,7-dihydrobenzofuro[6,5-*d*][1,3]dioxole-6-carboxamide **3l**, see the Supporting Information}.[17]

The product 2,3-dihydrobenzofurans could be further converted into the corresponding aromatic benzofurans, which is a privileged scaffold in various important natural products and show a wide range of biological activities.[18] Using DDQ as the oxidizing agent, 2,3-dihydrobenzofuran products **3a** and **3b** can be transformed smoothly to the desired aromatized products **4a** and **4b** with good yields according to the known literature method (Scheme 3).[19]

In conclusion, we have developed a facile method for the synthesis of 2,3-dihydrobenzofurans *via* the *o*-QMs *in situ* generated from readily available 2-alkyl-substituted phenols using silver oxide-mediated oxidation in good yields and excellent diastereoselectivity. In addition, 2,3-dihydrobenzofurans were conveniently converted to the aromatized 2,3-disubstituted benzofurans using DDQ as oxidant.

Experimental Section

General Procedure for the Synthesis of 2,3-Dihydrobenzofurans

A reaction mixture of 2-alkyl-substituted phenol **1** (0.24 mmol), sulfonium salt **2** (0.20 mmol), Ag_2O (111 mg, 0.48 mmol) and K_2CO_3 (33 mg, 0.24 mmol) in dichloromethane (3 mL) was stirred at room temperature for 12 h. Then water (20 mL) was added to the mixture. The organic layer was separated and the aqueous layer was extracted with dichloromethane (30 mL × 3). The combined organic layer was dried by anhydrous sodium sulfate, concentrated

under vacuum. The crude product was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate to give the corresponding *trans*-2,3-dihyrobenzofuran products **3**.

***trans*-{7-(4-Methoxyphenyl)-6,7-dihydrobenzofuro[6,5-*d*]-[1,3]dioxol-6-yl](phenyl)methanone (3a):** yield: 95%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.97$–7.87 (m, 2H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.14 (d, $J = 8.7$ Hz, 2H), 6.87 (d, $J = 8.7$ Hz, 2H), 6.55 (s, 1H), 6.42 (s, 1H), 5.94–5.85 (m, 2H), 5.76 (d, $J = 6.2$ Hz, 1H), 4.78 (d, $J = 6.2$ Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 195.0, 159.2, 153.8, 148.2, 142.7, 134.6, 134.0, 129.4, 129.2, 128.9, 120.6, 114.5, 105.2, 101.6, 93.4, 91.7, 55.5, 50.6; HR-MS: $m/z = 397.1031$, calculated for $C_{23}H_{18}NaO_5$ $[M+Na]^+$: 397.1052.

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[17] CCDC 945017 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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