ChemPubSoc Europe
DOI: 10.1002/ejoc.201501280
EurJOC European Journal of Organic Chemistry
Full Paper

Oxidative Coupling

Solvent and Temperature Effects on the Platinum-Catalyzed Oxidative Coupling of 1-Naphthols

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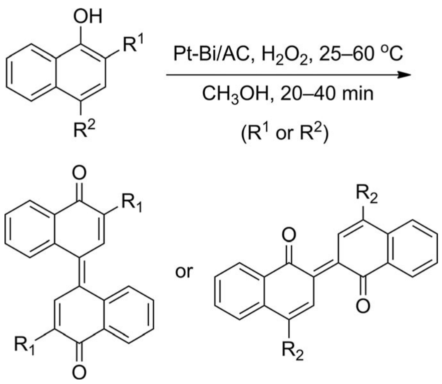
Abstract: Using H_2O_2 as the oxidant, 1-naphthols with electron-donating groups at the 2- and 4-positions couple oxidatively over a carbon-supported platinum catalyst to 3,3′-substituted 1,1′-binaphthalenylidene-4,4′-diones and 4,4′-substituted 2,2′-binaphthalenylidene-1,1′-diones, respectively. The binaphthalenyl diols are the intermediates. The selectivity to individual products is influenced by the reaction temperature (room temp. or reflux) and by the solvent used. Under reflux, complete conversions are obtained within 40 min. At room temp. high diol yields can be obtained, e.g. 96 % from 2-methyl-1-naphthol in MeOH. Under reflux the reaction proceeds always further to the diones (at least to some extent), and THF is a promising solvent for the selective one-pot two-step oxidation of 1-naphthols to the diones (e.g. 81 % from 4-methoxy-1-naphthol). In most other solvents (reflux) naphthoquinones are observed as byproducts. In an attempt to optimize the yield of menadione, 30.5 % was obtained in boiling $MeNO_2$.

Introduction

Aryl–aryl coupling and cross-coupling reactions[1] are efficient and reliable methods for the formation of new carbon–carbon bonds in organic synthesis. These reactions lead to the formation of coupled aromatic rings, and the biaryl or triaryl frameworks formed are central building blocks for a large number of natural products.[2] They are also useful for many pharmaceutical applications, as organic dyes and as ligands in enantioselective catalysis.[1,3] The following reaction patterns are commonly encountered: (i) oxidative coupling of various arenes, including metal phenolates by chemical, catalytic or electrochemical methods, (ii) coupling between aryl halides and aryl-metal species, and (iii) electrophilic arylation of quinone derivatives with hydroarenes in the presence of acids or bases.[2,4]

In order to limit the formation of by-products catalytic methods should gradually replace many of the stoichiometric procedures currently employed.[5] Recently we reported the use of bismuth-promoted platinum supported on activated carbon (5 %Pt-5 %Bi/AC) as a heterogeneous catalyst for the oxidative coupling of substituted 1-naphthols that contain electron-donating groups *para* or *ortho* to the hydroxyl group.[6] Depending on the substrate and the reaction conditions, the principal final products are the binaphthalenylidenediones (Scheme 1). Hydrogen peroxide, which is a green oxidant,[7] is used as the oxidizing agent.



Scheme 1. Oxidative coupling of 2- or 4-substituted 1-naphthols to the corresponding binaphthalenylidenediones (binaphthones) over promoted activated-carbon-supported platinum.

Oxidation and oxidative coupling reactions of naphthols are favored by an increase of the electron density on the aromatic system.[1,8] Therefore, charge transfer from external sources, such as solvents or catalysts, could play an important role in activating the substrate. Solvents are known to play a crucial role in liquid-phase catalysis; this is referred to as the "solvent effect".[9] Solvents can stabilize intermediates and thus influence the kinetics of a reaction. They are also able to modify the chemisorption of reactants and intermediates on the surface of heterogeneous catalysts.[9] In this way they are expected to influence the mechanism of a reaction. A decisive effect of solvents on the selectivity and performance of oxidation and oxidative coupling reactions has often been observed.[5,8,10] For example, in the oxidation of 2-methyl-1-naphthol to menadione with Ti-MMM-2 (mesoporous titanium-silicate) as the catalyst

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Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/ejoc.201501280.

and H_2O_2 as the oxidant, different solvents offer different selectivities:[10b] at 80 °C the yield of menadione obtained is 75 % in MeCN, 38 % in EtOAc, 27 % in AcOH and 17 % in MeOH. Menadione (vitamin K_3) is a blood coagulating agent and is also used as an intermediate for the preparation of other group K vitamins.[10b,11] The preparation of menadione from 2-methylnaphthalene by stoichiometric oxidation with CrO_3/H_2SO_4 is often used as an example for an industrial process that should be replaced by a more environmentally benign catalytic method.[7b,10b]

In this paper we report on the solvent effects observed in the platinum-catalyzed oxidative coupling of substituted 1-naphthols. The substrates chosen are 2-methyl-1-naphthol, 2-ethyl-1-naphthol, 4-methoxy-1-naphthol and 1,4-dihydroxynaphthalene. CH_2Cl_2, $MeNO_2$, MeCN, Me_2CO, MeOH and THF are used as solvents. Some of their properties are summarized in Table 1. The donor number (DN) is a measure of the solvent basicity (the ability to donate electrons).[12] The basicity increases with increasing DN. Solvents with a high DN are expected to increase the electron density of the solute, i.e. in our case they should render the naphthol substrate more susceptible to oxidation. The Lewis acidity of a solvent (its ability to accept electrons) increases with increasing acceptor number (AN).[12] A solvent with a high AN is able to withdraw electrons from a substrate, thus making it more susceptible to reduction. Surely, other factors like the solvent polarity, the dielectric constant and the solubility of the reactants will also affect the outcome of a reaction,[13] and it cannot normally be expected that the reactivity correlates with any single solvent parameter.

Table 1. Some properties of the selected solvents.[13]

Solvent	B.p. [°C]	Dielectric constant	Polarity	DN [kcal mol^{-1}]	AN
CH_2Cl_2	40.2	7.0	polar aprotic	1.0	20.4
$MeNO_2$	101.2	36.6	polar aprotic	2.7	20.5
MeCN	82.0	35.7	polar aprotic	14.1	18.9
Me_2CO	56.2	20.7	polar aprotic	17.0	12.5
MeOH	64.6	32.7	polar protic	19.0	41.5
THF	66.0	7.6	polar aprotic	20.0	8.0

Results and Discussion

Oxidation of 2-Substituted 1-Naphthols

Oxidation of 2-methyl-1-naphthol (**1a**) and 2-ethyl-1-naphthol (**1b**) over 5 %Pt-5 %Bi/AC with H_2O_2 as the oxidant gives mainly three types of compounds (Scheme 2): 3,3′-dialkyl-1,1′-binaphthalenyl-4,4′-diol (**2**), 3,3′-dialkyl-1,1′-binaphthalenylidene-4,4′-dione (**3**) and 2-alkyl-1,4-naphthoquinone (**4**).

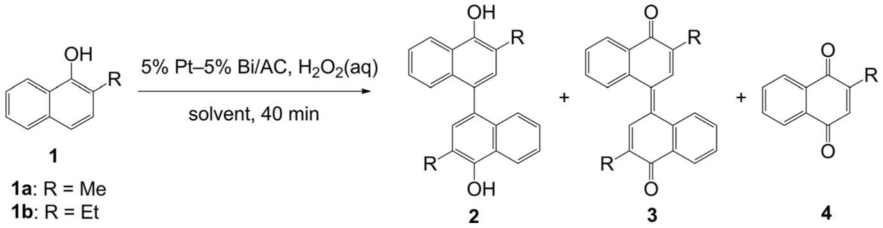
The selectivity is influenced by the substituent on the substrate, the solvent used and the reaction temperature. The results obtained are summarized in Table 2. Total conversions are achieved in all cases in which the reaction is carried out under reflux. Even at room temp. the less bulky methyl-substituted starting material (SM) is totally converted in $MeNO_2$ and MeOH, while conversions between 49 and 75 % are achieved in the other three solvents used (MeCN, Me_2CO and THF). The real issue of interest is therefore the selectivity of the reaction. In this regard, some common trends are observed for both substrates. At room temp. the binaphthols **2** are the major products. Independent of the conversion they are always formed with selectivities of 96–99.5 % (Table 2, entries 3, 5, 7, 10, 12 and 15) and the quinones **4** are not observed. However, apart from MeOH, in which traces of **4a** are found (entry 7), the only important exception is $MeNO_2$; $MeNO_2$ is unique in that it promotes the formation of considerable amounts of **4a** even at room temp. (22.5 % at 100 % conv.; Table 2, entry 1). Possibly for steric reasons, only trace amounts of **4b** are formed from the more bulky 2-ethyl compound (entry 12).

Table 2. Oxidative coupling of 2-alkyl-1-naphthols (**1**) and oxidation of binaphthols (**2**) over 5 % Pt–5 % Bi/AC in various solvents at room temp. or under reflux.

Entry	SM	Solvent	T [°C]	Conv. [%]	Selectivity [mol-%]			TOF (SM) [min^{-1}]
					2	**3**	**4**	
1	**1a**	$MeNO_2$	r.t.	100	62.1	trace	22.5	13.3
2[a]	**1a**	$MeNO_2$	96	100	51.2	trace	30.5	12.8
3	**1a**	MeCN	r.t.	49.2	99.2	trace	–	7.7
4	**1a**	MeCN	75	100	25.1	63.0	11.8	15.7
5	**1a**	Me_2CO	r.t.	73.0	99.5	trace	–	11.4
6[a]	**1a**	Me_2CO	52	100	15.1	60.7	12.8	13.9
7	**1a**	MeOH	r.t.	≤ 100	96.0	trace	trace	15.1
8	**1a**	MeOH	60	100	–	83.0	16.2	15.6
9[b]	**1a**	MeOH	60	100	1.4	86.4	11.7	16.3
10	**1a**	THF	r.t.	75.4	98.7	trace	–	11.7
11[c]	**1a**	THF	66	100	73.3	6.4	–	12.5
12	**1b**	$MeNO_2$	r.t.	73.2	99.0	trace	trace	11.4
13	**1b**	$MeNO_2$	96	≤ 100	57.6	trace	25.9	13.1
14[c]	**1b**	MeCN	75	≤ 100	35.3	27.9	21.8	13.3
15	**1b**	MeOH	r.t.	37.7	97.9	trace	–	5.8
16[c]	**1b**	MeOH	60	100	–	61.1	5.7	10.5
17	**2a**	MeOH	60	100	–	98.2	–	15.4
18	**2b**	MeOH	60	100	–	97.2	–	15.3

[a] Black deposits together with other by-products were formed. [b] Recycled catalyst containing 4.70 % Pt. [c] Two unknown compounds with similar retention factors could not be separated by column chromatography.

Under reflux, the selectivities shift from the binaphthols **2** to the binaphthones **3** as the major products. The bi-



Scheme 2. Oxidation of 2-alkyl-1-naphthols over a bismuth-promoted platinum catalyst.

naphthols are regarded as the intermediates to the binaphthones.[6] (Entries 17 and 18 in Table 2 confirm that the binaphthols convert readily and with high selectivity into the binaphthones.) For **1a**, at complete conversions, the selectivities to the binaphthone **3a** are 63, 61 and 83 % in boiling MeCN, Me_2CO and MeOH, respectively (entries 4, 6 and 8). In these reactions, apart from the intermediates **2**, the quinones **4** are the major by-products for both **1a** and **1b**. However, in MeOH no residual binaphthol is found (entries 8 and 16).

THF is exceptional in that both at room temp. and under reflux the binaphthol is formed with high selectivity and the quinone is not observed (entries 10 and 11). Similarly, $MeNO_2$ does not stimulate the formation of **3** (entries 2 and 13), but under reflux increased amounts of the corresponding quinones are obtained instead (31 and 26 % of **4a** and **4b**, respectively).

Figure 1 is a graphical illustration of the yields of **2a**, **3a** and **4a** obtained from 2-methyl-1-naphthol.

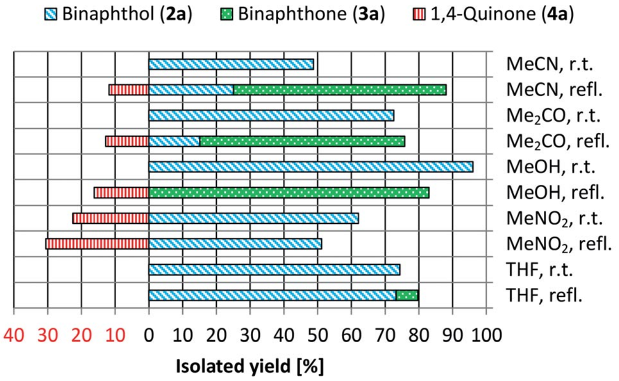


Figure 1. Yields of binaphthol **2a**, binaphthone **3a** and quinone **4a** obtained in various solvents from 2-methyl-1-naphthol (**1a**) at room temp. and under reflux.

As is obvious from Figure 2, **1a** and **1b** follow the same reaction patterns, but, possibly for steric reasons, the reactivity is somewhat lower for **1b**.

Entry 9 in Table 2 indicates that the catalyst can be recycled without any significant decline in activity. Due to a small loss of platinum during the first run (entry 8) the turn-over frequency (TOF) increases from 15.6 to 16.3 min^{-1}. In a control test no catalytic activity of leached metal was found.

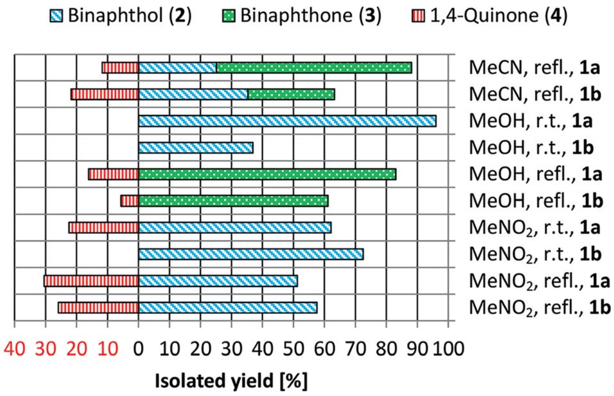


Figure 2. Yields of binaphthol **2**, binaphthone **3** and quinone **4** obtained from 2-methyl- (**1a**) and 2-ethyl-1-naphthol (**1b**) in three different solvents at room temp. and under reflux.

Formation of Menadione

As is evident from Figure 1, the highest yields of menadione (**4a**) are obtained in $MeNO_2$ as the solvent. Performing the reaction under dilute conditions should lower the concentration of the chemisorbed SM on the catalyst surface and suppress the formation of coupled products in favor of the quinone. Table 3 (entries 1–3) contains experiments performed at different concentrations of **1a** in $MeNO_2$ (conc. range: 0.507 to 0.085 mol/L). Starting with the highest concentration (entry 1), the selectivity to **4a** increases initially from 9.4 % to 30.5 % (entry 2), but then decreases again to 10.4 % (entry 3). In entry 1 appreciable amounts of **2a** are oxidized further to **3a**, whereas with declining concentration more and more **2a** desorbs from the catalyst unconverted. The formation of **3a** is a consecutive reaction, while the formation of **4a** competes with the synthesis of **2a**, but requires four times the amount of H_2O_2 per mol of SM (Scheme 3). It is therefore not surprising that at high dilution (entry 3) the limited availability of H_2O_2 favors the formation of

$$\begin{tikzcd}
(2)\ \text{H-Ar-OH} + H_2O_2 \arrow[r] \arrow[d, "+\,2\ H_2O_2"', "-\,3\ H_2O"] & \text{HO-Ar-Ar-OH} + 2\ H_2O \arrow[d, "+\,H_2O_2"', "-\,2\ H_2O"] \\
\text{O=Ar=O} & \text{O=Ar=Ar=O}
\end{tikzcd}$$

Scheme 3. Schematic illustration of the oxidation and oxidative coupling reactions of naphthols using H_2O_2. The stoichiometric factor 2 (in brackets) applies only to the horizontal reaction, not to the vertical reaction.

Table 3. Oxidation of 2-methyl-1-naphthol (6.34 mmol) in $MeNO_2$ under reflux (96 °C) using different substrate concentrations, varying amounts of H_2O_2 and varying amounts of catalyst.

Entry	Catalyst [g]	$MeNO_2$ [mL]	H_2O_2 [mmol]	Conversion [%]	Selectivity [mol-%]			TOF (SM) [min^{-1}]	TOF (H_2O_2) [min^{-1}]
					2a	**3a**	**4a**		
1	0.04	12.5	22	100	45.1	43.8	9.4	15.4	13.4
2[a]	0.04	25	22	100	51.2	–	30.5	12.8	13.6
3	0.04	75	22	100	89.3	–	10.4	15.7	10.3
4	0.04	100	88	100	68.9	–	29.6	15.5	14.7
5	0.04	25	66	100	2.6	80.6	6.5	14.1	14.9
6	0.02	25	22	84.7	95.6	–	trace	25.4	12.7

[a] Standard conditions: see entry 2 in Table 2.

2a rather than **4a**. This argument is in agreement with the total absence of **3a** in entries 2 and 3, as the conversion of **2a** to **3a** likewise calls for additional H_2O_2. Further, similar results are obtained in reactions carried out at different SM concentrations, but keeping the H_2O_2 concentration constant (entries 2 and 4).

In another experiment (entry 5), the amount of H_2O_2 added to the solution (in comparison to entry 2) was increased by a factor of three. Under these conditions almost all **2a** is oxidized further to **3a** (sel. 81 %), and little **4a** (6.5 %) is formed. Finally, when cutting the amount of catalyst used in half (entry 6), the reaction does not go to completion, **2a** is produced with high selectivity (96 %), and in comparison to entry 2 the reaction rate for the formation of **4a** is negligible.

It should be noted that all reaction steps in Scheme 3 produce water as the by-product. Therefore, they should be regarded as irreversible. Nevertheless, after all the SM has been converted, the product selectivity can still change, as any binaphthol can consume an equimolar amount of H_2O_2 and oxidize further to the binaphthone. Consequently, the productive usage of H_2O_2 would be a better measure of the reaction progress than the conversion of the SM. For this reason, TOFs based on H_2O_2 are included in Table 3. Identical values of the H_2O_2-based TOF correspond to the same reaction progress in terms of mol of H_2O_2 consumed for the formation of products. At a constant H_2O_2 uptake (entries 1 and 2) the selectivity to **4a** increases with dilution of the system. At even higher dilution (entry 3), the TOF of H_2O_2 decreases and mainly **2a** is formed, that is, a product requiring only 0.5 mol of H_2O_2 per mol of SM (Scheme 3). Similarly, at high H_2O_2 concentrations and identical H_2O_2 usage (entries 4 and 5), **4a** (29.6 %) is formed at low concentrations of the SM (entry 4), while mainly **3a** (80.6 %) is formed at high concentrations (entry 5).

Attention is drawn to the fact that quinone formation from **1** requires the transfer of one oxygen atom from H_2O_2 to the substrate, while oxidative coupling is basically a dehydrogenation reaction, and the role of the oxidant is limited to scavenging chemisorbed hydrogen from the surface of the metal catalyst.[6]

Remarkably, the formation of **4a** decreases with increasing donor number of the solvent (Figure 3). The same trend was extracted from the data provided by Kholdeeva et al.[10b] It seems therefore that charge transfer from the solvent to the substrate is not involved in the transition state of this reaction.

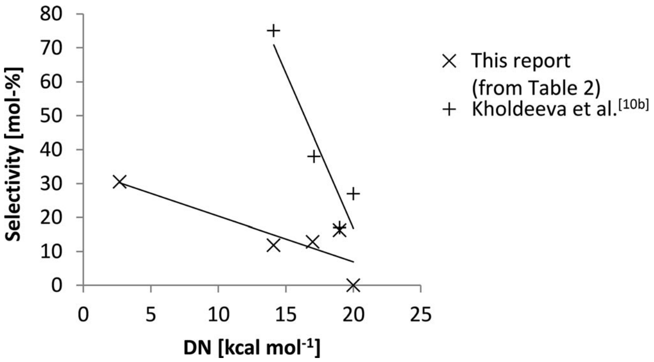
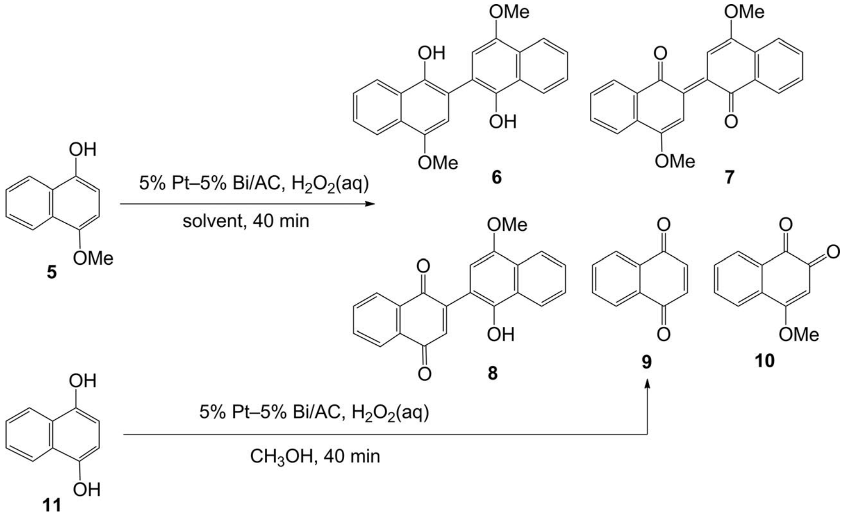


Figure 3. Selectivity to menadione at complete conversion of 2-methyl-1-naphthol plotted against the DN of the solvents used (reflux or 80 °C[10b]).

Oxidation of 4-Substituted 1-Naphthols

Substrate **5** (4-methoxy-1-naphthol) is the SM for a variety of different oxidation products (Scheme 4), namely 4,4′-dimethoxy-2,2′-binaphthalenyl-1,1′-diol (binaphthol **6**), 4,4′-dimethoxy-2,2′-binaphthalenylidene-1,1′-dione (Russig's blue or binaphthone **7**), 1′-hydroxy-4′-methoxy-2,2′-binaphthalenyl-1,4-dione (coupled naphthoquinone **8**), 1,4-naphthoquinone (**9**), and 4-methoxy-1,2-naphthoquinone (**10**). The products observed under our reaction conditions in different solvents at room temp. or under reflux are listed in Table 4, together with the corresponding conversions, selectivities and TOFs. Figure 4 is a graphical presentation of the yields obtained. As for **3a** and **3b**, the binaphthol must be regarded as the intermediate to the binaphthone.[6] Entry 11 in Table 4 shows that under reflux **6** can indeed be converted with a yield of 99.8 % to **7**.



Scheme 4. Oxidative coupling of 4-methoxy- (**5**) and 4-hydroxy-1-naphthol (**11**) over a bismuth-promoted platinum catalyst.

Table 4. Oxidation of 4-substituted 1-naphthols (**5**, **11**) and oxidation of binaphthol **6** over 5 % Pt–5 % Bi/AC in various solvents at room temp. or under reflux.

Entry	SM	Solvent	*T* [°C]	Conv. [%]	Selectivity [mol-%] **6**	**7**	**8**	**9**	**10**	TOF (SM) [min^{-1}]
1[a]	**5**	$MeNO_2$	r.t.	100	7.2	55.5	–	16.9	trace	12.5
2[a]	**5**	$MeNO_2$	96	100	–	67.1	–	20.7	1.3	14.0
3	**5**	Me_2CO	r.t.	69.8	98.0	–	–	–	trace	10.7
4	**5**	Me_2CO	52	100	–	85.4	–	10.2	trace	15.0
5	**5**	CH_2Cl_2	r.t.	100	63.9	35.5	–	–	–	15.6
6[a]	**5**	CH_2Cl_2	38	100	trace	67.0	17.4	–	–	13.3
7	**5**	MeOH	r.t.	100	–	62.0	trace	–	3.7	10.3
8	**5**	MeOH	60	100	–	–	81.0	–	–	12.7
9	**5**	THF	r.t.	26.1	trace	97.3	–	–	–	4.0
10	**5**	THF	66	100	14.0	81.0	–	–	–	14.9
11	**6**	THF	66	100	–	99.8	–	–	–	15.7
12	**11**	MeOH	r.t.	100	–	–	–	92.4	–	14.5
13	**11**	MeOH	60	100	–	–	–	95.2	–	15.0
14[b]	**11**	MeOH	60	58.0	–	–	–	41.9	–	–

[a] A violet-blue compound that appears to be a polymer was detected (^{13}C NMR) together with other by-products. [b] Blank reaction without catalyst.

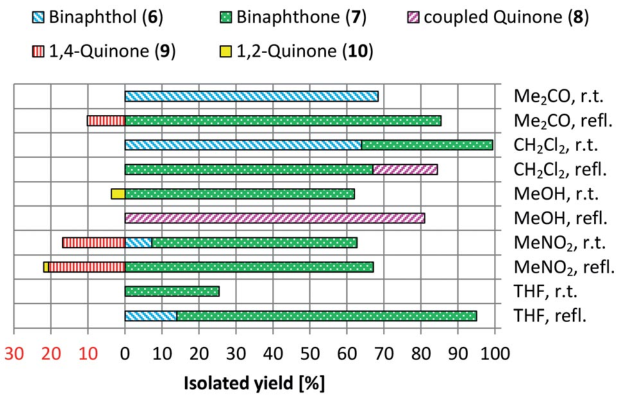


Figure 4. Product yields obtained from 4-methoxy-1-naphthol (**5**) in various solvents at room temp. and under reflux.

In contrast to substrates **1**, 4-methoxy-1-naphthol forms the binaphthone **7** even at room temp., most likely because the methoxy group is more electron-donating than alkyl groups. In fact, in THF (Table 4, entry 9) the intermediate binaphthol is completely converted into the binaphthone, but in this case the conversion of **5** is particularly low. In solution the binaphthol **6** is not entirely stable and slowly converts further to **7**, even in the absence of a catalyst. (UV/Vis spectroscopy of **6** in CH_2Cl_2 showed the characteristic absorption of **7** at $\lambda_{max} = 630$ nm after the solution was allowed to stand for 2 h.) As an exception, Me_2CO appears to stabilize **6**, and in this solvent **6** is the only product observed at room temp. (entry 3). Hence, in Me_2CO substrates **1** and **5** follow the same selectivity pattern. Some other observations are also similar to those found for the 2-alkyl-substituted 1-naphthol substrates:

- Under reflux complete conversions are obtained in all solvents tested.
- In THF no quinones are formed, even under reflux (entry 10).
- In $MeNO_2$ high amounts of naphthoquinones are formed at room temp. and under reflux (entries 1 and 2).

The naphthoquinone **8** is another type of coupling product that can be formed from **5**, but not from **1**.[6] It is observed as the major product (81 %) in refluxing MeOH (entry 8) and also as a by-product (17.4 %) in refluxing dichloromethane (entry 6). Like in THF, the naphthoquinones **9** and **10** are not formed in CH_2Cl_2.

A direct relationship between reactivity data and the solvent donor number could not be established. Takeya et al. noticed that for $SnCl_4$-mediated oxidative coupling reactions of 1-naphthol solvents with a low DN were particularly favorable.[10a] In our case a negative correlation between the selectivity to the coupled products **6** and **7** and the AN was found (Figure 5).

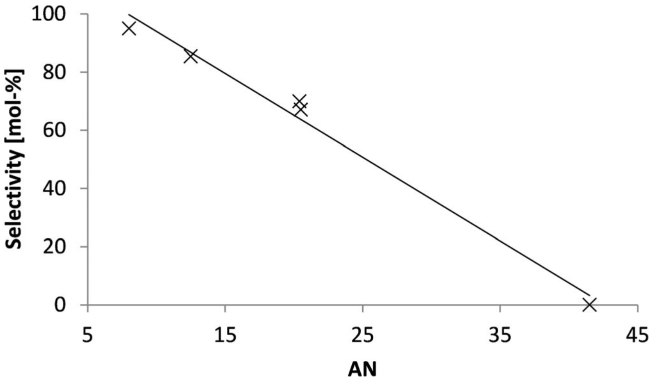


Figure 5. Selectivity to **6** + **7** at complete conversion of 4-methoxy-1-naphthol (from Table 4) plotted against the AN of the solvents used (reflux).

The reaction of 1,4-dihydroxynaphthalene (**11**) in MeOH (Scheme 4) gives **9** with selectivities of 92.4 and 95.2 % at room temp. and 60 °C, respectively (Table 4, entries 12 and 13). No coupling products are observed. This reaction also proceeds without a catalyst (entry 14), but with low conversion (58 %) and in an unselective manner (42 % of **9**, corresponding to a yield of 24 %). Over a platinum catalyst the reaction becomes a simple and selective dehydrogenation process [Equation (1)], similar to the conversion of the binaphthols to binaphthones (compare Scheme 3; Table 2, entries 17, 18; Table 4, entry 11).

$$HO–Ar–OH + H_2O_2 \rightarrow O{=}Ar{=}O + 2\ H_2O \qquad (1)$$

Conclusions

In the presence of hydrogen peroxide, 1-naphthols with electron-donating groups at the 2- and 4-positions couple oxidatively over a platinum catalyst to binaphthols. These can oxidize further to the corresponding binaphthones. The direct oxidation of the 1-naphthols to naphthoquinones competes with the coupling reaction. Apart from the substituent and the position of the substituent, the selectivity to the targeted products is influenced by the solvent and by the reaction temperature (room temp. or reflux). Among the SMs tested the reactivity follows the order **1b** < **1a** < **5**. Reactivity appears to increase with the electron-donating capacity of the substituents and to decrease with their steric demand. At room temp. the binaphthols (**2**) are obtained from **1a** and **1b** with high selectivity (96 to 99.5 %) in all solvents tested, except for $MeNO_2$. At room temp. binaphthone formation is not observed for **1**, but in case of the more reactive substrate **5**, the binaphthol (**6**) reacts further to the binaphthone (**7**). Under reflux conversions are always complete, the coupling reaction proceeds further to the binaphthones, and naphthoquinones are formed as by-products. In this regard, THF is exceptional in that it does not promote the formation of quinones. THF is therefore a promising solvent for the selective one-pot two-step oxidation of 1-naphthols to binaphthones (e.g. **1** to **3** or **5** to **7**). In striking contrast, $MeNO_2$ is the solvent of choice for quinone formation. $MeNO_2$ is the only solvent in which quinones form already at room temp. In refluxing $MeNO_2$ menadione can be obtained with a yield of 30.5 %.

In the case of substrate **5** two different final coupling products can form: the binaphthone (**7**) and the coupled naphthoquinone **8**. High yields of **8** are only obtained in boiling MeOH (≤ 81 %).

In separate reactions, the binaphthols (**2a**, **2b** and **6**) oxidize to the corresponding binaphthones (**3a**, **3b** and **7**). Under reflux yields of 97.2–99.8 % are readily obtained. This confirms that the binaphthols are the intermediates in the formation of the binaphthones. Likewise, 1,4-dihydroxynaphthalene (**11**) oxidizes to 1,4-naphthoquinone (yield: 95.2 %); no coupling products are observed in this case.

The catalyst can be recycled and the TOF for the reused catalyst remains above 15 min^{-1}. Any metal leached from the catalyst into solution does not contribute to the outcome of the reaction.

A positive correlation between reactivity data and the solvent donor number (DN), as might be expected for an oxidation reaction, was not found. However, the selectivity to **6** + **7** correlates negatively with the acceptor number. For the formation of menadione from **1a** a negative relationship between DN and the selectivity is indicated, not only for our own data, but also for the results provided by others. No other correlations between solvent properties and reaction data could be established. In particular, a relationship between the reaction temperature (determined by the boiling points of the solvents) and either conversion, TOFs or product selectivity was not found.

Our results show that solvent and temperature effects can be used to control the selectivity of a reaction system consisting of a consecutive and a parallel reaction. Individual products can be obtained with yields of up to 96 %. The system is truly catalytic and heterogeneous and has the potential to replace less environmentally benign stoichiometric methods.

Experimental Section

Materials and Catalyst: Activated carbon (Darko KB-G 174), bismuth(III) nitrate pentahydrate (98 %), hydrazine monohydrate (98 %), 1,4-dihydroxynaphthalene (99 %), 4-methoxy-1-naphthol (97 %), nitromethane (95 %) and silica gel for column chromatography (pore size 60 Å, 70–230 mesh, 63–200 µm) were purchased from Sigma–Aldrich. Hexachloroplatinic acid (metal content 40.31 %) was bought from SA Precious Metals. Hydrogen peroxide (30 %), acetone (99 %), acetonitrile (99.5 %), dichloromethane (99.5 %), ethyl acetate (99 %), methanol (99.5 %), petroleum ether (90 %) and tetrahydrofuran (99.5 %) were obtained from SMM Instruments, and Triton X-100 (98–102 %) from BDH. 2-Methyl-1-naphthol and 2-ethyl-1-naphthol were prepared as described previously.[6]

The 5 %Pt-5 %Bi/AC catalyst was prepared by dissolving $H_2PtCl_6{\cdot}6H_2O$ (0.1328 g, 0.2564 mmol Pt) and $Bi(NO_3)_3{\cdot}5H_2O$ (0.1162 g, 0.2396 mmol Bi) in 50 % H_2O/50 % MeOH (v/v, 100 mL). Triton X-100 (3 mL) was added. The mixture was placed in an ultrasonic bath for 2 h to dissolve the bismuth nitrate. The AC support (0.9005 g) was added and the mixture was stirred using a magnetic stirrer. After 10 min a 98 % aqueous solution of $N_2H_4{\cdot}H_2O$ (0.2 mL, 4.041 mmol N_2H_4) was added dropwise with a syringe to reduce the metal ions. Stirring continued for 28 h. After this the catalyst was filtered and washed with deionized water to pH 7. Finally it was washed with MeOH and dried at 140 °C for 24 h. The amounts of platinum and bismuth loaded onto the support were 4.91 and 4.89 %, respectively. Pt-Bi/AC catalysts are commercially available and these can be used to the same effect.[6]

Oxidation Reactions and Product Separation: Coupling reactions at room temp. or under reflux were carried out by placing the substrate (6.34 mmol) and the catalyst (0.0401 g) into a 100 mL round-bottomed flask, equipped with a condenser. A solvent (25 mL) was added. The mixture was stirred with a magnetic stirring bar. While stirring, 30 % aqueous H_2O_2 (3.1 mL, 22.1 mmol H_2O_2) was added over 40 min directly into the solution using a peristaltic pump. After the reaction the catalyst was separated by vacuum filtration, washed with CH_2Cl_2 and MeOH, and left to air-dry for possible reuse or analytical investigation. Column chromatography was used to separate the remaining reaction mixture (details given under product characterization). Product selectivities were calculated as mol percentages based on the mol of SM incorporated into each product (unconverted SM excluded). Isolated yields are reported as percentages of the theoretical yield. Turn-over frequencies (TOFs) are calculated as mol of SM incorporated into all identified products per mol of platinum present on the catalyst over the total reaction time (min^{-1}). In addition (Table 3), a TOF was calculated based on the theoretical quantity of mol of H_2O_2 required for total product formation.

Recycled catalysts were tested under conditions identical to those used for fresh catalysts, that is, the molar ratios of all reaction ingredients were kept constant in relation to the amount of the reused catalyst.

Testing for catalytic activity of leached metal was done as follows: a reaction (solvent: MeOH) was carried out as described above, but no SM was added. After 40 min the catalyst was filtered off and the coupling reaction was performed using only the solution (SM: **1a**).

(Only trace amounts of **2a** were found. The recovered catalyst contained 4.78 % Pt and 4.64 % Bi.)

Analytical Methods: Elemental analyses (Pt, Bi) were performed on a Spectro Arcos FHS ICP-OES instrument. FT-IR spectra were recorded from 4000 to 450 cm^{-1} on a Perkin–Elmer Spectrum Two universal attenuated total reflectance Fourier transform infrared spectrometer, equipped with KBr windows and a $LiTaO_3$ detector. The samples were mounted onto the diamond and a force gauge between 130 and 150 N was applied. A 400/54/ASP Varian 400 MHz premium-shielded NMR spectrometer was used to obtain ^{1}H NMR (100 MHz) and ^{13}C NMR (400 MHz) spectra. Maximum absorption wavelengths (λ_{max}) over the range from 200 to 700 nm were determined using a single beam Pharmacia Biotech Ultrospec 3000 UV/Visible spectrophotometer equipped with a tungsten filament lamp.

Characterization of the Organic Compounds: The characterization of 2-methyl-1-naphthol (**1a**), 2-ethyl-1-naphthol (**1b**), 3,3′-diethyl-1,1′-binaphthalenyl-4,4′-diol (**2b**), 3,3′-dimethyl-1,1′-binaphthalenylidene-4,4′-dione (**3a**), 4,4′-dimethoxy-2,2′-binaphthalenylidene-1,1′-dione (**7**), 1′-hydroxy-4′-methoxy-2,2′-binaphthalenyl-1,4-dione (**8**) and 4-methoxy-1,2-naphthoquinone (**10**) has been reported previously.[6] The ^{1}H NMR, ^{13}C NMR and IR spectra of **2a**, **4a**, **3b**, **4b**, **6** and **9** are contained in the supporting information. These compounds are described as follows.

3,3′-Dimethyl-1,1′-binaphthalenyl-4,4′-diol (2a): Violet solid, R_f = 0.92 (petroleum ether/ethyl acetate, 8:2); m.p. 247–248 °C. ^{1}H NMR (100 MHz, DMSO, 25 °C): δ = 2.37 (s, 6 H, 2 CH_3), 7.08 [d, ^{3}J(H,H) = 8.4 Hz, 2 H, $H^{3,3'}$], 7.14 [t, ^{3}J(H,H) = 7.6 Hz, 4 H, $H^{7,7',8,8'}$], 7.34 [t, ^{3}J(H,H) = 7.6 Hz, 2 H, $H^{6,6'}$], 8.23 [d, ^{3}J(H,H) = 8.8 Hz, 2 H, $H^{9,9'}$], 9.09 ppm (s, 2 H, 2 OH). ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 16.8 (CH_3), 117.9 ($C^{4,4'}$), 122.4 ($C^{9,9'}$), 124.9 ($C^{2,2'}$), 125.3 ($C^{3,3'}$), 125.6 ($C^{7,7'}$), 126.2 ($C^{10,10'}$), 129.5 ($C^{8,8'}$), 131.8 ($C^{6,6'}$), 132.6 ($C^{5,5'}$), 149.6 ppm ($C^{1,1'}$). IR (KBr): $\tilde{\nu}$ = 3468 cm^{-1} (OH).

2-Methyl-1,4-naphthoquinone (Menadione, 4a): Yellow needles, R_f = 0.97 (petroleum ether/ethyl acetate, 8:2); m.p. 104–105 °C. ^{1}H NMR (100 MHz, $CDCl_3$, 25 °C): δ = 2.17 (s, 3 H, CH_3), 6.81 (s, 1 H, H^{3}), 7.69–7.71 (m, 2 H, $H^{6,7}$), 8.02–8.09 ppm (m, 2 H, $H^{5,8}$). ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 16.44 (CH_3), 126.1 (C^{3}), 126.5 (C^{6}), 132.1 (C^{10}), 132.2 (C^{8}), 133.5 (C^{9}), 133.6 (C^{5}), 135.6 (C^{7}), 148.1 (C^{2}), 184.9 (C^{4}), 185.5 ppm (C^{1}). IR (KBr): $\tilde{\nu}$ = 1659 (CO), 1621 cm^{-1}.

3,3′-Diethyl-1,1′-binaphthalenylidene-4,4′-dione (3b): Solid with green metallic luster, R_f = 0.53 (petroleum ether/ethyl acetate, 9:1); m.p. 156–157 °C. ^{1}H NMR (100 MHz, $CDCl_3$, 25 °C): δ = 1.13 [t, ^{3}J(H,H) = 7.2 Hz, 6 H, 2 CH_3], 2.58 [q, ^{3}J(H,H) = 7.2 Hz, 4 H, 2 CH_2], 7.63 (s, 4 H, $H^{7,7',8,8'}$), 7.85–7.89 (m, 4 H, $H^{3,3',6,6'}$), 8.32–8.34 ppm (m, 2 H, $H^{9,9'}$). ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 13.01 (CH_3), 23.48 (CH_2), 127.8 ($C^{4,4'}$), 130.1 ($C^{6,6'}$), 130.6 ($C^{10,10'}$), 131.0 ($C^{8,8'}$), 132.3 ($C^{9,9'}$), 134.1 ($C^{5,5'}$), 137.5 ($C^{7,7'}$), 140.4 ($C^{2,2'}$), 141.6 ($C^{3,3'}$), 183.8 ppm ($C^{1,1'}$). IR (KBr): $\tilde{\nu}$ = 1614 cm^{-1} (CO).

2-Ethyl-1,4-naphthoquinone (4b): Yellow needles, R_f = 0.48 (petroleum ether/ethyl acetate, 8:2); m.p. 86–87 °C. ^{1}H NMR (100 MHz, $CDCl_3$, 25 °C): δ = 1.18 [t, ^{3}J(H,H) = 7.6 Hz, 3 H, CH_3], 2.58 [q, ^{3}J(H,H) = 7.2 Hz, 2 H, CH_2], 6.78 (s, 1 H, H^{3}), 7.70–7.72 (m, 2 H, $H^{7,8}$), 8.04–8.10 ppm (m, 2 H, $H^{6,9}$). ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 11.83 (CH_3), 22.62 (CH_2), 126.0 (C^{3}), 126.5 (C^{6}), 132.0 (C^{10}), 132.3 (C^{8}), 133.6 (C^{9}), 133.6 (C^{5}), 133.9 (C^{7}), 153.1 (C^{2}), 185.2 (C^{4}), 185.3 ppm (C^{1}). IR (KBr): $\tilde{\nu}$ = 1662 (CO), 1618 cm^{-1}.

4,4′-Dimethoxy-2,2′-binaphthalenyl-1,1′-diol (6): Light blue needles, R_f = 0.64 (*n*-hexane/ethyl acetate, 8:2); m.p. 218–220 °C. ^{1}H NMR (100 MHz, $CDCl_3$, 25 °C): δ = 3.91 (s, 6 H, 2 OCH_3), 6.88 (s, 2 H, $H^{3,3'}$), 7.46–7.53 (m, 4 H, $H^{7,7',8,8'}$), 8.08 [d, ^{3}J(H,H) = 8 Hz, 2 H, $H^{9,9'}$], 8.21 [d, ^{3}J(H,H) = 8 Hz, 2 H, $H^{6,6'}$], 8.89 ppm (s, 2 H, 2 OH). ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 56.09 (2 OCH_3), 107.9 ($C^{3,3'}$), 120.8 ($C^{2,2'}$), 121.7 ($C^{9,9'}$), 122.9 ($C^{6,6'}$), 125.6 ($C^{7,7'}$), 125.9 ($C^{8,8'}$), 126.2 ($C^{5,5'}$), 127.2 ($C^{10,10'}$), 142.9 ($C^{4,4'}$), 148.7 ppm ($C^{1,1'}$). IR (KBr): $\tilde{\nu}$ = 2583 cm^{-1} (The shift from 3400 cm^{-1} is due to the hydrogen bond between –OH and the oxygen on the methoxy group.[14]).

1,4-Naphthoquinone (9): Light yellow needles, R_f = 0.75 (*n*-hexane/ethyl acetate, 8:2); m.p. 120–122 °C. ^{1}H NMR (100 MHz, $CDCl_3$, 25 °C): δ = 6.95 (s, 2 H, $H^{2,3}$), 7.72–7.74 (m, 2 H, $H^{7,8}$), 8.04–8.06 ppm (m, 2 H, $H^{6,9}$). ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 126.3 ($C^{6,9}$), 131.8 ($C^{5,10}$), 133.8 ($C^{7,8}$), 138.6 ($C^{2,3}$), 184.9 ppm ($C^{1,4}$). IR (KBr): $\tilde{\nu}$ = 1656 (CO), 1605 cm^{-1}.

Acknowledgments

M. V. Maphoru is grateful for financial support by the Deutscher Akademischer Austauschdienst, DAAD-NRF bursary.

Keywords: C–C coupling · Oxidation · Platinum · Solvent effects

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Received: October 5, 2015
Published Online: November 20, 2015