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Copper-catalysed oxidative alkoxylation of acyl- and carbomethoxy-hydroquinones

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Abstract—Oxidation of title hydroquinones by an [O^2/Cu^ICl] system in the presence of alcohols yields (71–88%) corresponding regioselectively 3-alkoxylated compounds. Compared with the classical procedure (silver oxide oxidation) in which alcohols have to be added to intermediate quinones in a second step, leading to a 1:1 mixture of starting material and final quinones, this new selective one-pot system does not oxidize alcohols and regenerates intermediate quinones from starting hydroquinones. Moreover, in situ trapping of the unstable formyl-quinone now allows the preparation of its 3-alkoxy derivative.

1. Introduction

Despite the large occurrence of alkoxy-substituted quinonic compounds and their derivatives amongst natural products, studies about their synthesis through addition of alcohols onto quinones are somewhat rare.

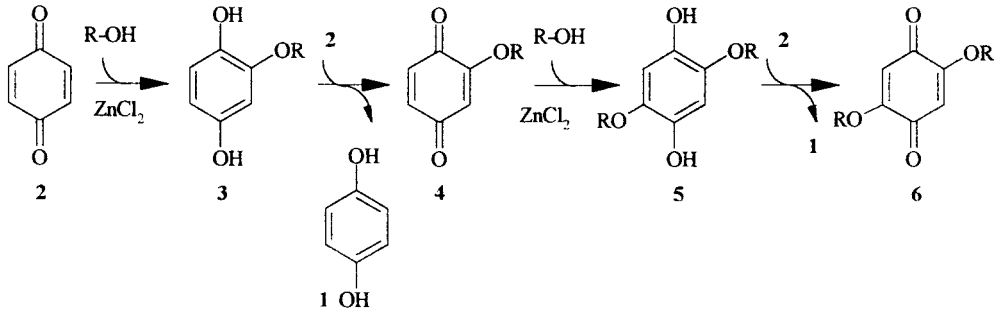
Alkoxylation of 1,4-benzoquinones is well known to require the presence of a Lewis acid catalyst since Knœvenagel's studies (Scheme 1).[1]

Indeed, addition of methanol or ethanol to 1,4-benzoquinone **2** proceeds in the presence of the Lewis acid catalyst $ZnCl_2$ (or $CaCl_2$, $MgCl_2$), and affords the corresponding 2,5-dialkoxy-benzoquinones **6**, together with two equivalents of hydroquinone **1**, the latter resulting from the redox reactions between intermediate alkoxy hydroquinones **3** and **5** and the starting benzoquinone **2**.

More recent studies[2] have shown that, in the absence of Lewis acid catalyst, moderate yields of mono-alkoxylated quinones (mixture of isomers) could be obtained through prolonged heating (48 h) of methyl-benzoquinone with ethanol.

On the other hand, 1,2-benzoquinones (e.g. **8**) are more sensitive towards nucleophilic addition. As a typical example, in situ oxidation of pyrocatechol **7** in the presence of CH_3OH leads to 4,5-dimethoxy-1,2-benzoquinone **9**, using lead tetraacetate[3] or a [Cu^{II} complex/O_2] system[4] as oxidant (Scheme 2).

We have previously shown that a [O_2/Cu^I/Cu°] system was able to successively *ortho*-hydroxylate phenols and dehydrogenate the resulting pyrocatechols into 1,2-benzoquinones which can then react with the starting phenol to afford aryloxy-quinones after further dehydrogenation.[5–9]



Scheme 1.

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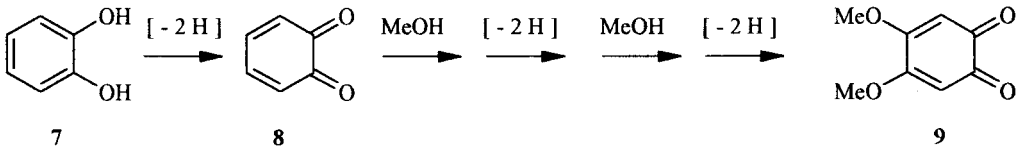
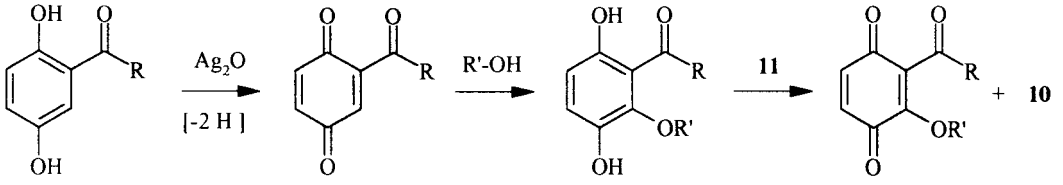


7 8 9

Scheme 2.



10 11 12 13

a) R = H

b) R = CH_3 R' = CH_3, C_2H_5, *i*-C_3H_7, *n*-C_4H_9, CH_2-CH=CH_2, *c*-C_6H_{11}, CH_2-C_6H_5

Scheme 3.

In the particular case of 4-methoxyphenol, the resulting 4-methoxy-5-(4-methoxyphenoxy)-1,2-quinone is amenable to selective substitutions of the aryloxy leaving group by a variety of alcohol[5–9] and amine[10] nucleophiles to give access to the synthesis of numerous additional quinonoid compounds. In particular, alkylation of the nucleus through Claisen–Cope reactions can be obtained after addition of allylic alcohols[5,9] and amines[11–14] onto this 1,2-quinone.

The reactivity of *para*-quinones is greatly enhanced when they are substituted by an electron-withdrawing group, as in formyl and acetyl compounds **11a**,**b**. Selective mono-addition of alcohols R′–OH on the activated carbon-3 position have thus been obtained in benzene, without addition of any Lewis acid catalyst, in the case of 2-acetyl-1,4-benzoquinone (**11b**) (Scheme 3).[15]

Quinone **11b** was prepared by silver oxide-mediated oxidation of 2-acetylhydroquinone **10b** in the presence of a desiccating agent ($MgSO_4$, Na_2SO_4) in 90–95% yield;[16–19] Quinone **11b** was then separated from the excess of Ag_2O to avoid oxidation of alcohol R′–OH, which is consequently added in a second step. The transient 3-alkoxy-hydroquinone **12b** is rapidly oxidised by the higher-potential unreacted quinone **11b**, and the alkoxylated quinone **13b** is finally obtained together with one equivalent of starting material **10b**, in a theoretical yield at the best equal to 50% (37–50% effective yield from quinone **11b**).

2-Formyl-1,4-benzoquinone (**11a**) is quite more reactive than **11b**; it can be obtained with difficulty through Ag_2O oxidation of **10a** in a very moderate yield of 32%,[20] and only thio[21] and azido[22] nucleophiles have yet been successfully added onto it, but not alkoxy ones.

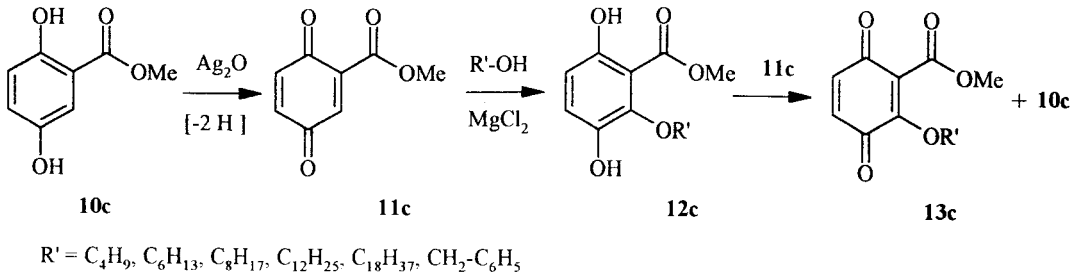
2-Carbomethoxy-1,4-benzoquinone (**11c**) is quite less reactive than **11b** thanks to its weaker electron-withdrawing 2-substituent. Hormi et al.[23] recently reported that the addition of alcohols to **11c** leads to 3-alkoxy-hydroquinones **12c** only in the presence of $MgCl_2$ as a Lewis acid catalyst in toluene solvent. One can here note the agreement with Knœvenagel's pioneering results.[1] Here also, since silver oxide is used as an oxidant, alcohols are added to quinone **11c** in a second step, and two equivalents of **11c** give rise to one equivalent of 3-alkoxy-quinone **13c** (effective yield=40–45%) along with one mole of starting material hydroquinone **10c**, as shown in Scheme 4.

The regioselective addition of various nucleophiles on the 3-carbon position of quinones **11a–c** was clearly ascribed by all the authors[15,21–23] to the electron-withdrawing character of the formyl, acetyl or carbomethoxy substituents on the 2-carbon position, which renders the 2,3 double bond more reactive than the 5,6 one. Additional conformational studies, based on redox potentials and spectroscopic data, showed that the preferred conformation of **11a** was planar, with the formyl carbonyl group *anti* to the 1-carbonyl, whereas acetyl group in **11b** and other more bulky acyl groups were approximately perpendicular to the quinonoid ring.[24] The effect of the most powerful electron-withdrawing formyl group is then enhanced by a favorable geometry, whereas the less withdrawing carbomethoxy is totally inefficient, presenting a non-planar conformation. Complexation of a bidentate chelating metal ion like Mg^{++} with the C(1)- and carbomethoxy-carbonyl groups[23] has therefore a double advantage; it establishes a more planar conformation and activates the system by acid catalysis.

2. Results

Having previously studied in our laboratory the oxidizing properties of the Cu^{II} complexes resulting from the reaction of $Cu^{I}Cl$ and molecular oxygen with simple phenol, pyrocatechol and hydroquinone substrates,[25,26] we were logically prompted to apply these conditions to the oxidative alkoxylation of the formyl-, acetyl- and carbomethoxy-hydroquinones **10a–c**.

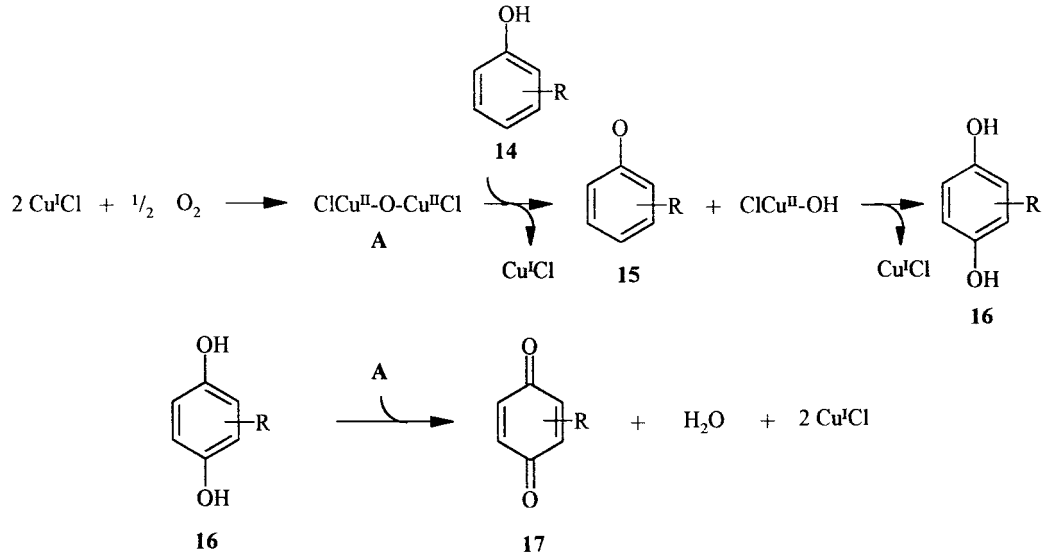
Basically, O_2 oxidises $Cu^{I}Cl$ in acetonitrile solution into a μ-oxo binuclear Cu^{II} complex **A**, which constitutes a simple chemical model of copper-enzymes *laccases*.[27] Electron-



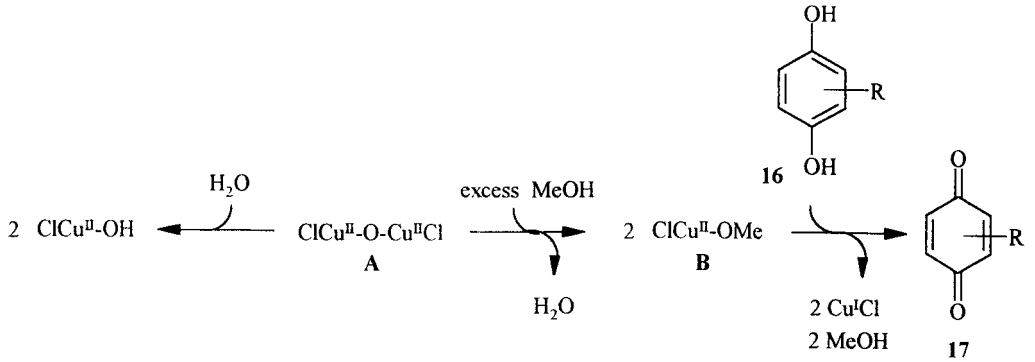
Scheme 4.

enriched phenols **14** (*R*=alkyl, alkoxy or *N*-acetamido groups) are hydroxylated by excess complex A into hydroquinones **16** by the intermediary of phenoxy radicals **15** through a succession of one-electron oxidations ('SET'), and the resulting hydroquinones are dehydrogenated into *para*-quinones **17** in a 80–85% global yield. Minor amounts of *ortho*-quinones possibly formed through *ortho*-hydroxylation of starting phenols have not been detected, since they are readily subject to nucleophilic additions (water, phenolic compounds) and further oxidations in these conditions. This sequence, in which $Cu^{I}Cl$ clearly plays a catalytical role with regard to the oxidant O_2, is described in Scheme 5.

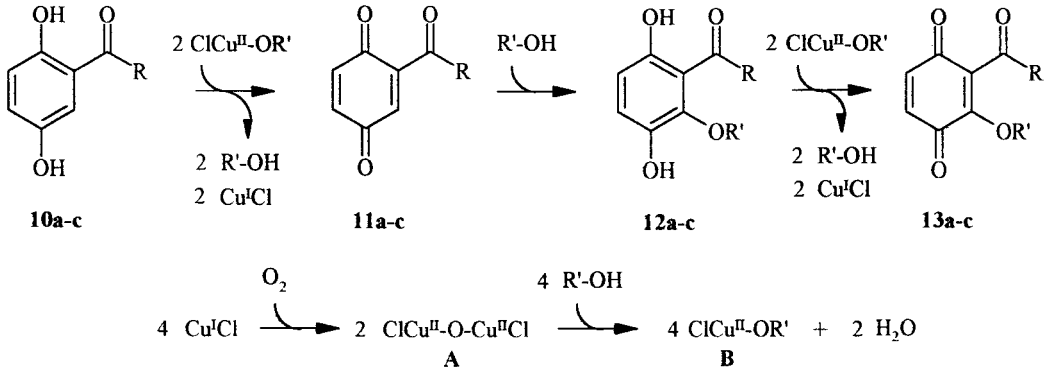
Involvement of phenoxy radical intermediates **15** has been inferred from the formation of dimers or polymers of the starting phenols, instead of quinones **17**, at low values of the ratio **A**/phenol; the coupling rate of these radicals is then superior to the rate of the oxidative –OH ligand transfer 15→16.[25,26] Such a behaviour is representative of one-electron oxidants such as $FeCl_3$, $K_3Fe(CN)_6$, Ag_2CO_3 and some Cu^{II} salts.[28]



Scheme 5.



Scheme 6.



Scheme 7.

As shown in Scheme 6, complex **A** reacts with water and alcohols to afford mononuclear species such as the methoxy complex **B** when **A** reacts with methanol;[25,26] this divalent copper complex **B** is also able to dehydrogenate hydroquinones into *para*-quinones.

It thus appeared that complexes of type **B** could be valuable candidates for the oxidative alkoxylation of hydroquinones **10a–c**, in the presence of an efficient desiccating agent in order to limit troublesome competition between H_2O and the alcohol R′–OH in the nucleophilic addition step **11a–c→12a–c** (Scheme 7).

The oxidant Cu^{II} complex **B** takes part in a catalytic process, being regenerated from $Cu^{I}Cl$ by oxidation (O_2) and alcoholysis (R′–OH) of intermediate A. H_2O is trapped by finely ground anhydrous $CaSO_4$ (Drierite®), which affords better results than Na_2SO_4 or $MgSO_4$. Once the oxidation completed, copper complexes are reduced down to metallic Cu^{O} by excess aqueous $Na_2S_2O_4$ and the products are recovered as stable alkoxy-hydroquinones **12a–c** since quinones **13a–c** are readily reduced under these conditions. It is important to ensure that the reduction of copper is complete, since traces of Cu^{I}/Cu^{II} may contaminate final product and cause its decomposition upon air exposure.

Hence, 2-formyl-hydroquinone (**10a**) reacted with methanol under these conditions to afford the 3-methoxy substituted compound **12a**, 2-acetyl-hydroquinone (**10b**) reacted with methanol, ethanol and benzyl alcohol to give 3-methoxy-acetylhydroquinone **12b1**, 3-ethoxy-acetylhydroquinone **12b2** and 3-benzyloxy-acetylhydroquinone **12b3**, respectively (Scheme 8). At last, 2-carbomethoxy-hydroquinone **10c** and *n*-hexanol directly gave 3-hexyloxy-carbomethoxy-hydroquinone **12c**, without any addition of a Lewis acid like $MgCl_2$.

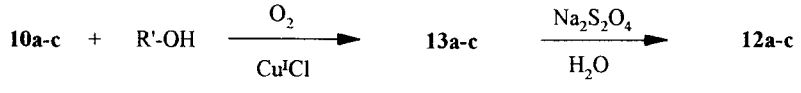
Oxidation of 2-formyl-1,4-hydroquinone (**10a**) with MeOH in MeCN at room temperature leads to poor yields of addition product **12a**, besides tarry materials; the reaction is preferably performed at 0°C, where the high reactivity of quinone **11a** towards nucleophilic reagents allows to reach completion in 2 h.

High-melting acetyl-hydroquinone (**10b**) requires first to be refluxed in a 1:1 mixture of MeCN-EtOAc for complete dissolution; the oxidation addition reaction is then performed at 20°C for 3 h (MeOH) to 5 h (BnOH). Ester **10c**, giving the less activated 2-carbomethoxy-1,4-quinone **11c**, needed to be reacted for 5 h at room temperature with n-hexanol in pure MeCN.

Increasing yields of the desired 3-alkoxy-hydroquinones **12a–c** (Scheme 8) are apparently obtained when decreasing the reactivity of the 2-acyl-quinones. This is plausibly due to the relative ease of H_2O addition onto the quinones **11a–c** and **13a–c**, since water is present as traces in the course of the oxidation, and even in much greater quantity during the final reduction step **13a–c→12a–c** with aqueous $Na_2S_2O_4$. It was also noted that, carbomethoxy-quinone **13c** is stable under silica gel TLC conditions;[23] this is not the case for acetyl-quinone **13b** and especially not for the formyl-quinone **13a**.

3. Conclusion

The use of the inexpensive copper/O_2 system as oxidant of hydroquinones **10a–c** instead of silver oxide brings another advantage in the fact that the alcohols R′–OH are not oxidized by Cu^{II} complexes **A** and **B**. A 'one-pot' procedure, in which quinones **11a–c** are thoroughly alkoxylated,



a) R = H R' = Me **12a** 71 %

b) R = CH_3 R' = Me **12b1** 85 % R' = Et **12b2** 87 % R' = CH_2-C_6H_5 **12b3** 79%

c) R = OCH_3 R' = n-C_6H_{13} **12c** 88 %

Scheme 8.

is thus permitted and avoids the wastage of half the starting hydroquinones **10a–c**.

Quinones **11a–c** are produced in the presence of alcohols R′–OH, and no longer in a preliminary step. The more reactive 2-formyl-hydroquinone **11a** is rapidly trapped and gives rise to the desired alkoxylated quinone **13a**, then to hydroquinone **12a**, so far inaccessible by this type of reaction.

The Cu^{II} ion in the complexes of this oxidant system behaves as a Lewis acid, and, like $MgCl_2$ in Hormi's work,[23] catalyses the addition of R′–OH onto the poorly reactive carbomethoxy-quinone **11c**, allowing the direct and efficient one-pot transformation of hydroquinone **10c** into 3-alkoxylated quinone **13c**.

4. Experimental

4.1. General

Melting points were determined on a Kofler (Reichert) apparatus; ^{1}H NMR spectra were obtained with internal standard $SiMe_4$ on a Bruker AC 300 spectrometer (300 Mhz).

Oxidations are carried out under an oxygen atmosphere in a 250 ml round-bottomed flask, fitted with a magnetic stirrer and a water or ice/water bath. Acyl-hydroquinones **10a**,**b** and cuprous chloride are of 98–99% pure commercial quality. MeCN, 99.5% pure commercial quality, $H_2O<0.1\%$, is used without further purification. Anhydrous $CaSO_4$, Drierite®, is purchased from W. A. Hammond Drierite Co.

Monitoring of the oxidation is performed through reduction of a little sample (~0.05 ml) by $Na_2S_2O_4$ in water and extraction with EtOAc. The organic phase is then analysed by thin layer chromatography on silica gel (pre-coated silica gel $60F_{254}$ aluminium sheets, Merck). Alkoxy-substituted hydroquinones **12a–c** are all eluted faster than the corresponding starting compounds **10a–c** (typically R_f=0.5 and 0.4 with an EtOAc:cyclohexane=4:6 eluant mixture).

4.1.1. 2-Formyl-3-methoxy-hydroquinone (12a). *Procedure A.* To a cooled (0°C) solution of 1.38 g (0,01 mol) 2-formyl-hydroquinone (2,5-dihydroxybenzaldehyde) **10a** and 3 ml (0.075 mol) methanol in dry MeCN (40 ml), stirred with anhydrous powdered $CaSO_4$ (20 g) under a dioxygen atmosphere, are added 3.96 g (0.04 mol) Cu(I)Cl; conditions are maintained for 2 h, then toluene (60 ml) is added and MeCN distilled off under reduced pressure. The resultant slurry is diluted with 150 ml EtOAc, the liquid phase separated by filtration on a Celite® layer and stirred with an aqueous solution (70 ml) of 6 g $Na_2S_2O_4$ and 0.6 g $NaHCO_3$ until metallic copper precipitates, then washed again with a solution of $Na_2S_2O_4$ (1.5 g). After drying over $MgSO_4$, the solvents are evaporated under reduced pressure to afford 1.09 g **12a** (0.0065 mol, 65% yield). As yellow crystals, mp 80–82°C, mp lit.[29] 85–86°C. ^{1}H NMR ($CDCl_3$+DMSO d_6): δ (ppm) 4.0 (s, 3H), 6,4 (d, 1H, J=9 Hz), 7.2 (d, 1H, J=9 Hz), 7.9–9.1 (broad, 1H), 10.2 (s, 1H), 10.8–11.1 (broad, 1H).

Procedure B. 2-Formyl-hydroquinone **10a**, 1.38 g (0.01 mol), is dissolved in dry MeCN (40 ml) with 3 ml (0.075 mol) MeOH, then stirred with anhydrous powdered $CaSO_4$ (20 g) under a dioxygen atmosphere at 0°C, and 3.2 g (0.032 mol) Cu(I)Cl are added. Conditions are maintained for 2 h, then an aqueous solution (100 ml) of 10 g $Na_2S_2O_4$ and 2 g $NaHCO_3$ is added to the reaction mixture. After overnight stirring, the resultant slurry is extracted with 4×150 ml EtOAc, and the organic phase rinsed with 15 ml saturated brine. After drying over $MgSO_4$, the solvents are evaporated under reduced pressure to afford 1.2 g **12a** (0.0071 mol, 71% yield).

4.1.2. 2-Acetyl-3-methoxy-hydroquinone (12b1). 2-Acetyl-hydroquinone **10b**, 1.52 g (0.01 mol), is totally dissolved through refluxing in dry MeCN (40 ml) and co-solvent EtOAc (40 ml) with 3 ml (0.075 mol) MeOH, then stirred with anhydrous powdered $CaSO_4$ (20 g) under a dioxygen atmosphere at 20°C, and 3.2 g (0.032 mol) Cu(I)Cl are added. Conditions are maintained for 3 h, then an aqueous solution (100 ml) of 10 g $Na_2S_2O_4$ and 2 g $NaHCO_3$ is added to the reaction mixture. After overnight stirring, the resulting slurry is extracted with 3×150 ml EtOAc, and the organic phase rinsed with 15 ml saturated brine. After drying over $MgSO_4$, the solvents are evaporated under reduced pressure to afford 1.55 g **12b1** (0.0085 mol, 85% yield). As yellow crystals, mp 90–91°C mp lit.[15,30–32] 90°C. ^{1}H NMR ($CDCl_3$): δ(ppm) 2.75 (s, 3H), 3.88 (s, 3H), 5.40 (s, 1H), 6.70 (d, 1H, J=9 Hz), 7.20 (d, 1H, J=9 Hz), 12.10 (s, 1H).

4.1.3. 2-Acetyl-3-ethoxy-hydroquinone (12b2). 2-Acetyl-hydroquinone **10b**, 1.52 g (0.01 mol), is dissolved under warming in dry MeCN (40 ml) and co-solvent EtOAc (40 ml) with 3 ml (0.05 mol) EtOH, then stirred with anhydrous powdered $CaSO_4$ (20 g) under a dioxygen atmosphere at 20°C, and 3.2 g (0.032 mol) Cu(I)Cl are added. Conditions are maintained for 3 h, then an aqueous solution (100 ml) of 10 g $Na_2S_2O_4$ and 2 g $NaHCO_3$ is added to the reaction mixture. After overnight stirring, the resultant slurry is extracted with 3×150 ml EtOAc, and the organic phase rinsed with 15 ml saturated brine. After drying over $MgSO_4$, the solvents are evaporated under reduced pressure to afford 1.70 g **12b2** (0.0087 mol, 87% yield). As yellow crystals, mp 103–104°C, mp lit.[15] 102–103.5°C. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.51 (t, 3H, J=7 Hz), 2.75 (s, 3H), 4.10 (q, 2H, J=7 Hz), 5.20 (s, 1H), 6.60 (d, 1H, J=9 Hz), 7.12 (d, 1H, J=9 Hz), 11.90 (s, 1H).

4.1.4. 2-Acetyl-3-benzyloxy-hydroquinone (12b3). 2-Acetyl-hydroquinone **10b**, 1.52 g (0.01 mol), is dissolved under warming in dry MeCN (40 ml) and co-solvent EtOAc (40 ml) with 4.32 g (0.04 mol) benzyl alcohol, then stirred with anhydrous powdered $CaSO_4$ (20 g) under a dioxygen atmosphere at 20°C, and 3.2 g (0.032 mol) Cu(I)Cl are added. Conditions are maintained for 5 h, then an aqueous solution (100 ml) of 10 g $Na_2S_2O_4$ and 2 g $NaHCO_3$ is added to the reaction mixture. After overnight stirring, the resultant slurry is extracted with 3×150 ml EtOAc, and the organic phase rinsed with 15 ml saturated brine. After drying over $MgSO_4$, the solvents are evaporated under reduced pressure and the residue crystallized from Et_2O/hexane to separate excess benzyl alcohol and afford 2.05 g **12b3** (0.079 mol, 79% yield). As yellow crystals, mp

90–91°C, mp lit.[15] 87.5–89°C, mp lit.[33] 94°C (from petroleum ether). ^{1}H NMR ($CDCl_3$): δ (ppm) 2.70 (s, 3H), 4.95 (s, 2H), 5.25 (s, 1H), 6.70 (d, 1H, J=9 Hz), 7.10 (d, 1H, J=9 Hz), 7.38 (s, 5H), 11.90 (s, 1H).

4.1.5. 2-Carbomethoxy-3-hexyloxy-hydroquinone (12c). To a cooled (0°C) solution of 1.68 g (0.01 mol) methyl 2,5-dihydroxybenzoate **10c**[34] and 4.08 g (0.04 mol) *n*-hexanol in dry MeCN (40 ml), stirred with anhydrous powdered $CaSO_4$ (20 g) under a dioxygen atmosphere, are added 3.96 g (0.04 mol) Cu(I)Cl; conditions are maintained for 1 h, and the mixture warmed-up to 20°C for 4 h, always stirred under O_2. 60 ml toluene are then added and MeCN distilled off under reduced pressure. The resultant slurry is diluted with 150 ml EtOAc, the liquid phase separated by filtration on a Celite® layer and stirred with an aqueous solution (70 ml) of 6 g $Na_2S_2O_4$ and 0.6 g $NaHCO_3$ until metallic copper precipitates, then washed again with a solution of $Na_2S_2O_4$ (1.5 g). After drying over $MgSO_4$, the solvents are evaporated under reduced pressure together with 100 ml xylene in order to sweep off the excess of *n*-hexanol. The crystalline crude product is finally dried under vacuum (0.1 mmHg) to yield 2.37 g **12c** (0.088 mol, 88%). As colourless crystals, mp 57–58 °C, lit.[23] 57°C. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.90 (t, 3H), 1.33 (m, 4H), 1.47 (m, 2H), 1.82 (m, 2H), 3.88 (t, 2H), 3.99 (s, 3H), 5.54 (s, 1H), 6.72 (d, J=9.0 Hz), 7.13 (d, J=9.0 Hz), 10.57 (s, 1H).

References

1. Knœvenagel, E.; Bückel, C. *Berichte* **1901**, *34*, 3993–3998.
2. Singh, J. M.; Turner, A. B. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2556–2559.
3. Wanzlick, H.-W.; Jahnke, U. *Chem. Ber.* **1968**, *101*, 3744–3752.
4. Rogic, M. M.; Demmin, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 5472–5487.
5. Reinaud, O.; Capdevielle, P.; Maumy, M. *Tetrahedron Lett.* **1985**, *26*, 3993–3996.
6. Reinaud, O.; Capdevielle, P.; Maumy, M. *Synthesis* **1987**, 790–794.
7. Reinaud, O.; Capdevielle, P.; Maumy, M. *Tetrahedron Lett.* **1987**, *28*, 4675–4678.
8. Reinaud, O.; Capdevielle, P.; Maumy, M. *Tetrahedron* **1987**, *43*, 4167–4176.
9. Reinaud, O.; Capdevielle, P.; Maumy, M. *Synthesis* **1988**, 293–300.
10. Viallon, L.; Reinaud, O.; Capdevielle, P.; Maumy, M. *Synthesis* **1995**, 1534–1538.
11. Viallon, L.; Reinaud, O.; Capdevielle, P.; Maumy, M. *Tetrahedron Lett.* **1995**, *36*, 4787–4790.
12. Viallon, L.; Reinaud, O.; Capdevielle, P.; Maumy, M. *Tetrahedron Lett.* **1995**, *36*, 6669–6672.
13. Viallon, L.; Reinaud, O.; Capdevielle, P.; Maumy, M. *Tetrahedron* **1996**, *52*, 7841–7854.
14. Viallon, L.; Reinaud, O.; Capdevielle, P.; Maumy, M. *Tetrahedron* **1996**, *52*, 13605–13614.
15. Farina, F.; Valderrama, J. *Synthesis* **1971**, 315–316.
16. Woroshzow, N. N.; Mamaew, V. P. *Sb. Statei Obshch. Khim.* **1953**, 533–535.
17. Kloetzel, M. C.; Dayton, R. P.; Abadir, B. Y. *J. Org. Chem.* **1955**, *20*, 38–47.
18. Abdulla, K. A.; Abdul-Rahman, A. L.; Al-Hamdany, R.; Al-Saigh, Z. Y. *J. Prakt. Chem.* **1982**, *324*, 498–504.
19. Mathur, P.; Dismukes, G. C. *J. Am. Chem. Soc.* **1983**, *105*, 7093–7098.
20. Bruce, J. M.; Creed, D. *J. Chem. Soc. C* **1970**, 649–653.
21. Ruiz, V. M.; Tapia, R.; Valderrama, J.; Vega, J. C. *J. Heterocycl. Chem.* **1981**, *18*, 1161–1164.
22. Cassis, R.; Fernandez, M.; Tapia, R.; Valderrama, J. A. *Synth. Commun.* **1987**, *17*, 1077–1088.
23. Hormi, E. O. E.; Moilanen, A. M. *Tetrahedron* **1998**, *54*, 1943–1952.
24. Bruce, M.; Heatley, F.; Ryles, R. G.; Scrivens, J. H. *J. Chem. Soc., Perkin Trans. 2* **1980**, 860–866.
25. Capdevielle, P.; Maumy, M. *Tetrahedron Lett.* **1983**, *24*, 5611–5614.
26. Capdevielle, P.; Maumy, M. *L'Actualité Chimique* **1986** (Avril), 5–11.
27. Multicopper enzymes of the fungal laccase type oxidise phenols into dimers, polymers or *para*-quinonoid compounds through one-electron reactions: Solomon, E. I.; Sundaram, U. M.; Machonkin, T. E. *Chem. Rev.* **1996**, *96*, 2563–2605.
28. Wedemeyer, K.-F. In *Methoden der Organischen Chemie (Houben–Weyl)*, Müller, E., Ed.; Georg Thieme: Stuttgart, 1976; Vol. VI/1c-2, pp 1121–1129 and references therein.
29. Merchant, J. R.; Naik, R. M.; Mountwalla, A. J. *J. Chem. Soc.* **1957**, 4142–4143.
30. Baker, W. *J. Chem. Soc.* **1939**, 956–961.
31. Wallenfels, K. *Chem. Ber.* **1942**, *75*, 785–793.
32. Nagarajan, G. R.; Rani, U.; Parmar, V. S. Isolation from leaves of Fraxinus floribunda Wall. *Phytochemistry* **1980**, 2494–2495.
33. Baker, W.; Brown, N. C.; Scott, J. A. *J. Chem. Soc.* **1939**, 1922–1927.
34. Methyl 2,5-dihydroxy-benzoate (**10c**) was prepared by $MeOH/H_2SO_4$ esterification of commercial 2,5-dihydroxybenzoic acid according to: Corey, E. J.; Kigoshi, H. *Tetrahedron Lett.* **1991**, *32*, 5025–5028.