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Selective Monoetherification of 1,4-Hydroquinone Promoted by $NaNO_2$

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Abstract: Catalytic amounts of $NaNO_2$ are able to successfully promote the reaction between 1,4-hydroquinone and methanol under acidic conditions, affording selectively the corresponding mequinol in excellent isolated yields. According to the proposed reaction mechanism, the semi-quinone intermediate, generated in situ from the corresponding hydroquinone by NO_2 oxidation, is the real reactive species, undergoing nucleophilic attack onto the alcoholic molecule. Experimental evidences emphasize the key role of NO_2. After optimization of the reaction conditions, the scope of the proposed protocol is extended to a wider range of alcohols, providing the corresponding mono-ethers in good to excellent yields. Moreover, when substituted hydroquinones are selected as reactive substrates, monoetherification occurs with complete regio-selectivity towards the less hindered phenolic –OH group.

Keywords: Etherification, Alkylation, Hydroquinones, Semiquinone.

INTRODUCTION

Monoethers of 1,4-hydroquinone, and in particular mequinol and monobenzone, are products of great interest from both an industrial and a biological point of view. The monomethyl ether of 1,4-hydroquinone, commonly named mequinol, is an important building block which is also used as antioxidant for edible oils and greases, polymerization inhibitor for acrylic compounds, stabilizer for photo sensitive materials, lubricating additive for high-temperature gas turbine engine oils, and key intermediated in many pharmacological applications [1].

Historically, monoethers are prepared by means of the Williamson Reaction, which consists in the reaction of a halide with an alkoxide or an aroxide [2]. Besides this approach, many synthetic protocols have been developed, based on the selective monoetherification of hydroquinone derivatives.

In 1900, Russig reported the first conversion of naphthoquinones into monoalkylated ethers of the corresponding naphthohydroquinones. The Russig-Laatsch procedure consists in the initial reduction of quinone with sodium dithionite followed by reaction with an alcohol saturated with HCl [3]. An alternative approach, based on the use of dimethylsulfate in a two-phase system in the presence of sodium hydroxide, allowed to obtain mequinol in up to 80 % yield [4].

More recently, ion-exchanged zeolites have been used to promote the selective *O*-methylation of hydroquinone by methanol [5]. In this protocol, the selectivity depends on the zeolite's basicity and on the operating temperature, which is generally maintained above 200 °C.

It was found that high selectivity towards mono-alkylation of 1,4-hydroquinone could be obtained in the presence of catalytic quantities of *p*-benzoquinone. Following this simple approach, many companies were able to develop processes for the production of mequinol on industrial scale. In the 70th Kodak Eastman patented the direct mono-*O*-methylation of 1,4-hydroquinone by methanol in the presence of catalytic amounts of sulfuric acid and *p*-benzoquinone [6]. Hereafter, Enichem Synthesis developed a new process in which the catalyst *p*-benzoquinone was produced *in-situ* from hydroquinone in the presence of H_2O_2 [7]. Moreover, in 2005 Yadav *et al*. reported the use of various heteropolyacids supported on montmorillonite to achieve mequinol from hydroquinone and methanol [8]. Even if it appears evident that the presence of *p*-benzoquinone is crucial in the above mentioned protocols in order to afford the desired products in good yields, its role in the reaction mechanism is still controversial. Yadav and co-workers [8] suggested an ionic mechanism according to which protonated methanol adds to a protonated benzoquinone chemisorbed on the heterogeneous catalyst. However, while this mechanism emphasizes the adsorption role of the heterogeneous acidic catalyst, it does not explain the real function of benzoquinone under homogeneous conditions. Furthermore, according to the proposed mechanism, it is not clear why di-substitution does not occur. It is well known that 1,4-hydroquinone (HQ) and *p*-benzoquinone (BQ) generate an equilibrium reaction in solution, affording two molecules of the corresponding semiquinone intermediate (SQ) (Scheme **1**) [9].

We suggest that the *in situ* generation of semiquinone could play a key role in the reaction. On the basis of this mechanism interpretation, we here report a new protocol for the selective monoetherification of hydroquinone promoted by tiny amounts of $NaNO_2$ in acidic methanol (Scheme **2**). The optimized conditions are extended with success to a wider range of alcohols, proving the scope of the reaction.

EXPERIMENTAL SECTION

All starting materials were purchased from commercial suppliers without further purification. All reactions were performed under atmosphere of nitrogen. An Agilent 6890 Gas Cromatograph (GC) system equipped with a 30mt x 0.250mm HP-5MS GC column and an Agilent 5973 Mass Selective Detector (MSD) detector were used to identify the reaction products. NMR spectra were recorded at 400 MHz for ^{1}H and 100 MHz for ^{13}C. ^{1}H NOESY analyses were conducted on a Bruker 500 MHz spectrometer, setting the mixing time

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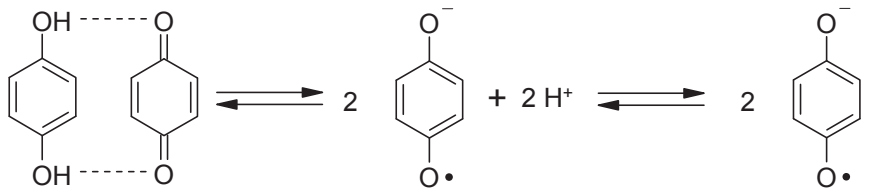
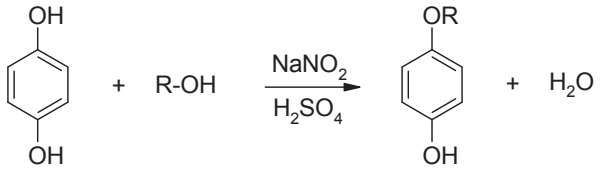


Scheme 1. Formation of semiquinone from 1,4-hydroquinone and *p*-benzoquinone.



Scheme 2. Monoetherification of HQ catalyzed by $NaNO_2$.

Table 1. Synthesis of mequinol from 1,4-hydroquinone and methanol in the presence of $NaNO_2$ and H_2SO_4[a]

#	Acid	$NaNO_2$ (mmol)	T (°C)	t (h)	Conv. (%)	Sel. (%)
1	H_2SO_4 (10 mmol)	0.5	r.T.	1	100	>99
2	H_2SO_4 (1 mmol)	0.5	r.T.	3	20	>99
3	H_2SO_4 (1 mmol)	0.5	r.T.	24	100	>99
4	-	0.5	r.T.	24	0	-
5	H_2SO_4 (10 mmol)	-	r.T.	24	0	-
6	H_2SO_4 (10 mmol)	0.5	reflux	1	100	< 30
7[b]	H_2SO_4 (10 mmol)	-	r.T	24	100	99
8[b]	H_2SO_4 (10 mmol)	-	reflux	4	100	96
9[c]	H_2SO_4 (100 mmol)	5	r.T.	1	100	>99

Experiments carried out under N_2 athmosphere. [a] 10 mmol of hydroquinone in 20 mL of methanol at room temperature. [b] 0.5 mmol of benzoquinone were employed in place of $NaNO_2$. [c] 100 mmol of hydroquinone in 50mL of methanol at room temperature. Conversions and yields determined by GC-MS.

at 300 ms, temperature at 298 K, sweep width at 10 ppm and the TD in F1 dimension at 512.

General procedure in the presence of $NaNO_2$: Hydroquinone (10 mmol), H_2SO_4 (98 %, 10 mmol) and $NaNO_2$ (0.5 mmol), were stirred in 20 ml of alcohol at room temperature and under N_2 atmosphere for the times reported in Tables **1** and **2**. The mixture was poured in water (100 mL) and extracted with $CHCl_3$ (100 mL x 3 times). The organic phase was dried with Na_2SO_4 and the solvent evaporated under vacuum providing hydroquinone monoether **3** crystals. The crude product was further purified by flash chromatography onto silica-gel (40-63 μm) using hexane:ethyl acetate (85:15 (v:v)) as eluent, affording **3** as the first eluted product (R_f = 0.35 on analytical TLC).

Similar experiments were performed using solid acidic catalyst (Amberlyst® A15 and Amberlite® IR120) in place of H_2SO_4, as detailed in Tables **2** and **3**.

Conversion and selectivity were determined by GC-MS analysis by sampling 100μL of the reaction mixture before the work-up, adding 2,6-dimethyl-1,4-benzoquinone as internal standard and diluting with $CHCl_3$. Yields of isolated products are based on the starting hydroquinones.

Monoalkyl ethers were identified by GC-MS and NMR spectroscopy by comparison with authentic samples.

General procedure in the presence of NO_2: Hydroquinone (10 mmol) and acidic catalyst (solid catalyst (2 g) or H_2SO_4 (98 %, 10 mmol) were added to 20 mL of methanol under N_2 atmosphere and the solution was maintained under magnetic stirring at the temperatures reported in Tables **3**. NO_2 was produced in a separate three necked round bottom flask (purged with N_2 before NO_2 production) by adding drop wise a solution of $NaNO_2$ (7.2 mmol - 0.5 g, in 5 mL of water) in 5 mL of 50 % H_2SO_4 aqueous solution over a time of 30 minutes. The produced red vapors were directly bubbled into the reaction mixture through a porous silica diffuser and the mixture was allowed to react for the times reported in Table **3**. The mixture was filtered, if required to remove the solid catalyst, poured in water (100 mL) and extracted with $CHCl_3$ (100 mL x 3 times). Mequinol **3a** and BQ were identified according to the procedures previously described.

RESULTS AND DISCUSSION

In order to optimize the reaction conditions, we initially focused our attention onto the monomethylation of hydroquinone **2a** (HQ) to mequinol **3a** (MQ, Scheme **2** R = CH_3) starting from methanol **1a** as alkylating agent. The results are reported in Table **1**.

When operating at room temperature, the H_2SO_4/$NaNO_2$ system led to a complete conversion in just 1 hour with 100 % selectivity in mequinol (Table **1**, entry 1) and no decomposition was observed even after 24 hours, showing how, under these mild conditions, the product is stable and the reaction is easily controllable. On the contrary, when the same reaction was conducted at reflux, tars were

Table 2. Synthesis of mequinol from 1,4-hydroquinone and methanol in the presence of $NaNO_2$ and solid catalyst[a]

#	Solid acid	$NaNO_2$ (mmol)	T (°C)	t (h)	Conv. (%)	Sel. (%)
1	A15	0.5	r.T.	24	100	90
2	A15	0.5	reflux	4	100	96
3	A15	-	r.T.	24	0	-
4	A15	-	reflux	4	0	-
5[b]	A15	-	reflux	4	50	93
6	IR120	0.5	r.T.	24	100	95
7	IR120	0.5	reflux	4	100	97
8	IR120	-	r.T.	24	0	-
9	IR120	-	reflux	4	0	-
10[b]	IR120	-	reflux	4	38	98

Experiments carried out under N_2 athmosphere. [a] 10 mmol of hydroquinone and 2g of solid acidic catalyst in 20 mL of methanol. [b] 0.5 mmol of benzoquinone were employed in place of $NaNO_2$. Conversions and yields determined by GC-MS.

mostly recovered even after just 1 hour (Table **1**, entry 6). The amount of H_2SO_4 was chosen in order to maintain an equimolar ratio between HQ and acid. By reducing the H_2SO_4 quantity up to 10 % with respect to HQ, the reaction run slower (Table **1**, entry 2) and a complete conversion was achieved only after 24 hours (Table **1**, entry 3), while no products were recovered in the absence of acid or $NaNO_2$ (Table **1**, entries 4 and 5).

Moreover, when the reaction was carried out using a higher amount of HQ (100 mmol in place of 10 mmol) and a reduced volume of methanol (Table **1**, entry 9), a complete conversion was observed with a selectivity similar to that reported under diluted conditions. This result shows the potential of this protocol, proving how it can be reproduced on larger scales.

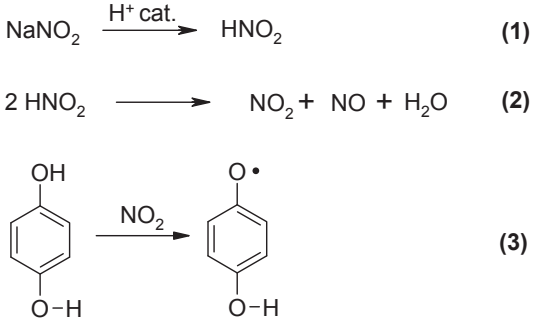
When BQ was employed in place of $NaNO_2$ at room temperature, the complete conversion was reached only after 24 hours, while an increase of temperature up to reflux of methanol allowed to achieve complete conversion and selectivity in just 4 hours (Table **1**, entry 7).

Commercially available Amberlyst 15 and Amberlite IR120 were also used as solid acidic catalysts (Table **2**). Both consist in a strongly acidic styrene-based sulfonated polymer bearing about 4.5 meq/g of $-SO_3H$ groups. As expected, the homogeneous reaction in the presence of H_2SO_4 was faster than the reactions catalyzed by solid acids (Table **2**, entries 1, 6), whereas no products were recovered in the absence of $NaNO_2$ (Table **2** entries 3, 4, 8, 9).

The experiments catalyzed by H_2SO_4 in which BQ was used in place of $NaNO_2$ gave complete conversion and high selectivity after longer reaction times (Table **1**, entries 7, 8), whereas lower conversions were observed in the presence of solid catalysts (Table **2**, entry 10).

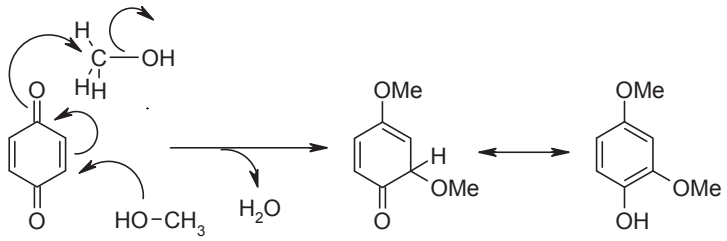
In conclusion, by operating under milder conditions the $H_2SO_4/NaNO_2$ system showed a higher efficiency in terms of conversion, selectivity, product stability and reaction time if compared with the heterogeneous systems, the latter requiring longer reaction times to afford, in any case, a lower selectivity.

The proposed mechanism involves the initial formation of semiquinone radical (SQ) from the corresponding hydroquinone by the oxidation in the presence of catalytic amounts of $NaNO_2$. According to Scheme **3**, under acidic conditions $NaNO_2$ affords HNO_2 *in situ* (Eq. 1); the latter rapidly decomposes forming NO_2 (Eq. 2) which in turn is able to efficiently oxidize HQ to SQ [10]. Working at room temperature, the decomposition of $NaNO_2$ to NO_2 is enough fast to efficiently promote the oxidation HQ to SQ, avoiding, at the same time, further Michael substitution, which leads to the formation of the corresponding 2,4-methoxy phenol (Scheme **4**). This product was observed with BQ when operating in the presence of solid catalysts.



Scheme 3. Semiquinone generation promoted by $NaNO_2$ under acidic conditions.

To confirm our hypothesis of mechanism, a set of experiments were performed in which NO_2 was used in place of $NaNO_2$ (Table **3**). In these cases, NO_2 was produced in a separate round bottom flask by decomposition of $NaNO_2$ in acidic medium and directly bubbled into the reaction mixture during its development. The experiments were performed either using H_2SO_4 or A15 or IR120 as acidic catalysts (Table **3**). The decomposition of $NaNO_2$ by H_2SO_4 was achieved by adding drop wise the solution of $NaNO_2$ in a 50 % H_2SO_4 solution, over a time of 30 minutes. The red NO_2 vapors so formed were directly bubbled into the reaction mixture through a porous silica diffuser. During the bubbling period the reaction solution turned dark due to the formation of BQ. In all the experiments **3a** was achieved as major product, this confirming the intervention of NO_2 in the reaction mechanism. Anyway lower conversions were observed compared to the reactions performed in the presence of $NaNO_2$, probably due to the gas-liquid mass transfer resistance. In



Scheme 4. 2,4-dimethoxy phenol formation mechanism.

Table 3. Synthesis of mequinol in the presence of NO_2 and solid catalyst[a]

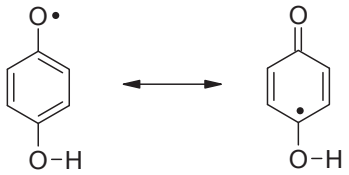
#	Acid Catalyst	T (°C)	t (h)	Conv. (%)	Sel. (%)
1	H_2SO_4 (10 mmol)	r.T.	1	77	90
2	IR120 (2g)	r.T.	24	45	96
3	IR120 (2g)	Reflux	4	34	94
4	A15 (2g)	Reflux	4	45	93

Experiments carried out under N_2 athmosphere. [a] 10 mmol of hydroquinone and acid catalyst in 20 mL of methanol.; 0.5 g of $NaNO_2$ in 5 mL of H_2O drop wise added to 5 ml of 50% H_2SO_4. Conversions and yields determined by GC-MS.

the presence of H_2SO_4 the reaction was fast even at room temperature. Nevertheless, the selectivity was slightly lower than the reactions in the presence of solid catalysts, and BQ was observed as by product (Table **3**, entry 1). In the presence of solid catalysts, BQ was the main by-product (Table **3**, entries 2), while low amounts of Michael adduct (less than 2 %) were found in the reactions carried out at reflux (Table **3**, entries 3 and 4).

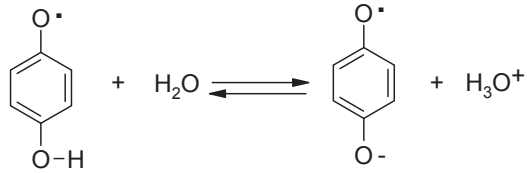
An experiment was also performed by reacting resorcinol (1,3-dihydroxybenzene) in place of HQ under the same conditions of experiment listed in Table 1, entry 1. Resorcinol should be not able to form the corresponding semiquinone and, as expected, no products were recovered after 24h.

The SQ radical presents two important characteristics: the bond dissociation energy for the O-H bond (54 kcal/mol is significantly lower than that in the corresponding diphenol (81 kcal/mol) while its acidity is extremely higher (pK_a = 4.0) compared to that of HQ (pK_a = 9.9) [11]. The lower dissociation energy for the O-H bond in semiquinone is explained by the conjugation of the unpaired electron with the aromatic ring (Scheme **5**).



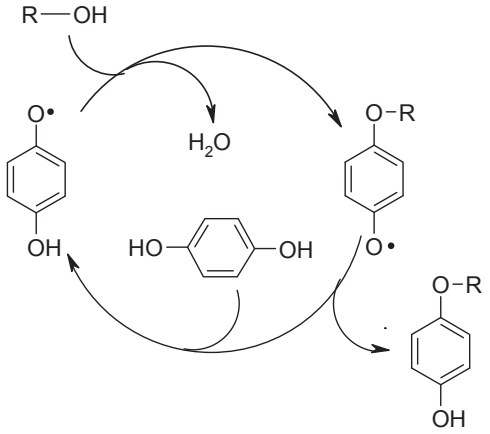
Scheme 5. Delocalization of unpaired electron of semiquinone.

The slightly high acidity of semiquinone is strictly connected with its low dissociation enthalpy. The pk_a value of SQ radical, analogous to that of acetic acid, suggests an occurring acid-base equilibrium which leads to the formation of a radical-anion intermediate under mild acidic or alkaline conditions (Scheme **6**).



Scheme 6. Acid-base dissociation reaction of semiquinone.

As carboxylic acids, which are easily esterified by reaction with alcohols in acidic medium, the radical adduct can also attack the alcohol affording the mequinol radical species. The latter undergoes hydrogen atom abstraction from a pristine hydroquinone leading to the formation of the final desired product and a new SQ molecule, which prolongs the radical chain (Scheme **7**).



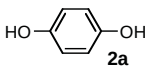
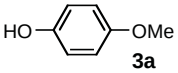
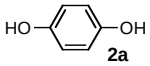
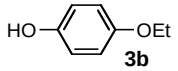
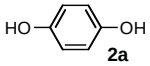
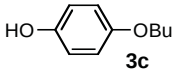
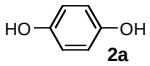
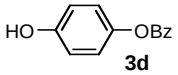
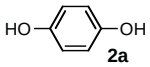
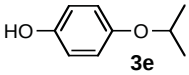
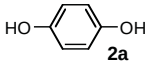
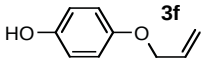
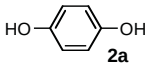
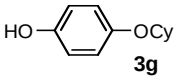
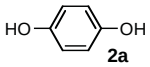
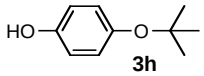
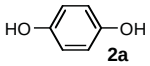
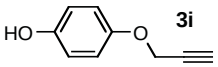
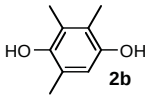
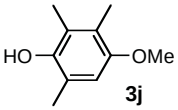
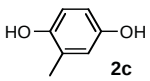
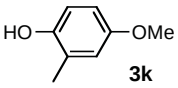
Scheme 7. Monoether formation mechanism.

In accordance with the proposed mechanism, further *O*-alkylation of the remaining free OH group does not occur and no traces of diethers are observed even after complete conversions, as monoalkyl ether is less acidic than corresponding semiquinone radical and is not able to reacts with alcohols.

Therefore, this protocol was successfully applied to several alcohols, as shown in Table **4**. In the experiments with benzyl alcohol and cyclohexanol, acetonitrile was used as co-solvent in order to obtain an homogeneous solution.

In the presence of benzyl alcohol (Table **4**, entry 4) an increase of the reaction time led to higher conversions, but with a lower selectivity due to the competitive formation of dibenzyl ether. In the presence of *tert*-butanol (Table **4**, entry 8) the low selectivity has to be ascribed to the formation of high amounts of BQ as principal by-product, while the reaction conducted with propargyl alcohol (Table

Table 4. Monoetherification of hydroquinone with different alcohols in the presence of $NaNO_2$ and H_2SO_4.

#	Alcohols	Quinone	T °C	t (h)	Conv. (%)	Sel. (%)	Products	Isolated Yield (%)
1	Methanol **1a**	 **2a**	rt	1	100	>99	 **3a**	92
2[a, 12]	Ethanol **1b**	 **2a**	rt	3	100	93	 **3b**	89
3[13]	1-Butanol **1c**	 **2a**	rt	72	95	>99	 **3c**	86
4[b, 14]	Benzyl alcohol **1d**	 **2a**	rt	24	87	86	 **3d**	75
5[15]	*iso*-Propanol **1e**	 **2a**	rt	24	95	>99	 **3e**	85
6[16]	Allyl alcohol **1f**	 **2a**	rt	24	99	98	 **3f**	90
7[b, 17]	Cyclohexanol **1g**	 **2a**	rt	48	90	>99	 **3g**	80
8	*tert*-Butanol **1h**	 **2a**	rt	48	48	63	 **3h**	22
9	Propargyl alcohol **1i**	 **2a**	rt	3	100	45	 **3i**	39
10[c]	Methanol **1a**	 **2b**	rt	3	100	70	 **3j**	63
11[c]	Methanol **1a**	 **2c**	rt	3	100	87	 **3k**	78

Experiments carried out under N_2 athmosphere. [a] 7 % of benzoquinone is formed; [b] 10 mL of CH_3CN were added to increase solubility; [c] confirmed by ^1H NMR NOESY analysis. Conversions and selectivities determined by GC-MS.

4, entry 9) led to the formation of the desired product **3i** in a moderate yield despite a relevant amount of tars was observed.

The etherification of substituted hydroquinones like 2,3,5-trimethyl- (Table **4**, entry 10) and 2-methyl-1,4-hydroquinones (Table **4**, entry 11) was also investigated. In both cases a total conversion was observed with good isolated yields of the desired monoethers. Anyway, the selectivity was lower than the corresponding un-substituted HQ mainly due to the formation of BQ and over-oxidized by-products as evidenced by GC-MS analysis. In spite of the asymmetry of the substrates, which would suggest the formation of two possible isomers, in both cases the reaction led to the formation of unique products with complete regio-selectivity. The monoethers structures were identified by 2D ^1H NOESY analysis (see supplementary information). As evidenced by the correlation between the methyl-ether and the two aromatic hydrogens in the case of **2k** and between the aromatic hydrogen and the near methyl group in the case of **3j**, both the etherifications underwent onto the less hindered phenolic –OH.

CONCLUSION

Mono-ethers of hydroquinone are of particular interest both for industrial and biological applications. The reaction of hydroquinone with alcohols, in the presence of catalytic quantities of benzoquinone and acids, gives the corresponding monoethers with both high yields and selectivities. The acidic behavior of the semiquinone specie provides, in the reaction media, the nucleophilic semiquinone, which attack the alcohol affording the mono-*O*-alkylated product. Higher selectivities toward the mono-*O*-alkylation are observed when semiquinone is generated *in-situ* through oxidation of hydroquinone by $NaNO_2$, via intermediate formation of NO_2. The

reactions occur under mild conditions (room temperature and atmospheric pressure of nitrogen), preventing the formation of Michael by-products onto *p*-benzoquinone. The possibility to extend the procedure on a wide range of alcohols and on substituted hydroquinones, together with the excellent results achieved by operating at 10 times larger scale, makes this protocol an intriguing alternative for the synthesis of mono-ethers of hydroquinones in high yields and selectivity under very mild conditions.

CONFLICT OF INTEREST

The author(s) confirm that this article content has no conflict of interest.

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SUPPLEMENTARY MATERIAL

Supplementary material is available on the publishers Web site along with the published article.

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