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Facile and highly efficient method for the C-alkylation of 2-hydroxy-1,4-naphthoquinone to nitroalkenes under catalyst-free 'on water' conditions

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ABSTRACT

C-Alkylation of 2-hydroxy-1,4-naphthoquinone to various nitroolefins was achieved under catalyst-free employing 'on water' conditions. The mechanism for the formation can be explained on the basis of dual activation of nitroalkene and 2-hydroxy-1,4-naphthoquinones via hydrogen bonding. Simple reaction conditions, high yields of the products, and environmentally benign medium are attractive features of this method.

Water is the most economical and environmentally benign solvent in the world. It exhibits unique reactivity and selectivity which are different from those of the conventional organic solvents.[1] Recently, reactions of water-insoluble organic compounds that occur in aqueous suspensions ('on water') have received a great deal of attention because of their high efficiency and straightforward synthetic protocols.[2] The advantages of conducting organic reactions 'on water' can be attributed due to the enhancement in rate and efficiency, ease of operation, and improved safety profile owing to the excellent heat capacity of water.[2f] From the green chemistry perspective, highly efficient and environmentally benign synthetic methodology is often regarded as a goal in modern organic chemistry. Thus, development of an efficient and convenient synthetic methodology employing 'on water' conditions is the subject of interest in the recent days.

Quinone and naphthoquinone moieties are prevalent motifs in various natural products which are associated with diverse biological activities.[3] Among the naphthoquinones, 2-hydroxynaphthoquinone derivatives are the molecules of interest as pigments[4] and biological entities.[5] Besides, they serve as potential synthetic precursors of carbocyclic and heterocyclic quinones, including 5*H*-benzo[*b*]carbazole-6,11-diones,[6] naphtho[2,3-*b*]furan-4,9-diones[7], and benzo[*b*]naphtha[2,3-*d*] furan-6,11-diones.[8] In particular, the derivatives of C-alkylated 2-hydroxynapthoquinones possess inhibitory effects on Epstein-Barr virus early antigen (EBV–EA) activation,[9] in vitro activity against the parasites such as *Toxoplasma gondii* and *Plasmodium falciparum*.[10] Lapachol and Atovaquone are two important compounds of C-alkylated 2-hydroxynapthoquinone derivatives, which exhibit numerous biological activities such as antibacterial, antiplasmodial, antioxidant, antimicrobial, antiprotozoal, antimalarial, trypanocidal, and anti-HIV.[11] In perspective of their important biological features in medicinal chemistry, a large number of quinone derivatives and related compounds have been synthesized in order to explore the novel bioactive agents with enhanced pharmacological properties.

The C-alkylation of nitroolefins with various electron-rich donors is the well-known C–C bond forming reaction. The Michael or Friedel–Crafts adduct of nitroalkanes obtained can be further transformed into diverse functionalities. In particular, the conjugate adducts derived from naphthoquinone and nitroalkenes serve as important building blocks for several bioactive molecules.[12] To our knowledge, very few methods have been reported for this transformation which includes the use of base[12] and organocatalyst.[13] In continuation of our interest on the development of green synthetic methodologies[14], herein we wish to report an efficient and catalyst-free protocol for the C-alkylation of 2-hydroxynaphthoquinone.

At the outset of our study, our attention was mainly focused to develop a catalyst-free system for the C-alkylation of 2-hydroxy-1,4-naphthoquinone with nitroolefins. With this in mind, we choose to examine the C-alkylation of 2-hydroxy-1,4-naphthoquinone **1** with the Michael acceptor 1-methyl-4-(2-nitrovinyl) benzene **2e** as the model substrates to establish the reaction conditions (Table 1). Initially, the reaction was conducted under solvent-free conditions, which resulted in poor yields of the Michael adduct (entry 1). Further, the fate of the reaction was examined with various organic solvents including toluene, tetrahydrofuran, ethanol, acetonitrile, and *N*,*N*-dimethyl formamide. Significantly, lower product yields were obtained for the perspective reaction in toluene, tetrahydrofuran, and ethanol (entries 2–

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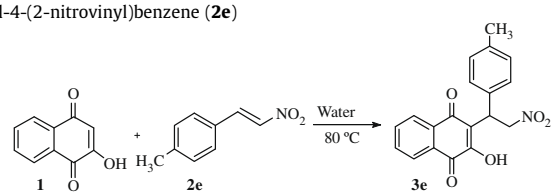
Table 1
Solvent screening for the C-alkylation of 2-hydroxy-1,4-naphthoquinone with 1-methyl-4-(2-nitrovinyl)benzene (**2e**)



Entry	Solvent	Temp (°C)	Time (h)	Yields[a,b] (%)
1	Neat	80	24	20
2	Toluene	80	24	30
3	THF	65	24	45
4	EtOH	80	24	55
5	MeCN	80	24	70
6	DMF	80	16	92
7	H_2O	25	24	40
8	H_2O	80	12	97

[a] All the reactions were conducted in 1 mmol scale.
[b] Yields were determined from crude ^{1}H NMR spectra using toluene as internal standard.

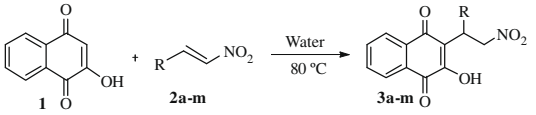
4). In contrast, improved yields were obtained in acetonitrile and *N*,*N*-dimethyl formamide which may be due the presence of trace amounts of water in the solvent. However, lower yields of the products were accomplished with anhydrous acetonitrile and *N*,*N*-dimethyl formamide. On the other hand, we tested the alkylation reaction employing 'on water' conditions and found that this was the best in terms of yields and conversion in shorter reaction times (Table 1, entry 8). Hence, 1.0 equiv of 2-hydroxy-1,4-naphtho quinone **1** was reacted with 1.2 equiv of 1-methyl-4-(2-nitrovinyl)benzene **2e** under catalyst-free conditions on water at 80 °C affording 2-hydroxy-3-(2-nitro-1-*p*-tolylethyl) naphthalene-1,4-dione **3e** in moderate to good yields. Having established the optimal reaction conditions, a wide range of nitroalkenes were treated with 2-hydroxy-1,4-naphthoquinone under the optimized reaction conditions to obtain the corresponding 2-hydroxy-3-(2-nitro-1-arylethyl) naphthalene-1,4-dione derivatives.[16] The results are summarized in Table 2.

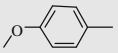
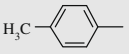
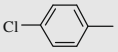
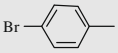
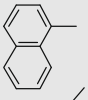
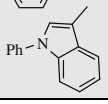
As can be seen from the Table 2, the Michael addition of 2-hydroxy-1,4-naphthaquinone proceeded well with various nitroolefins (**2a–m**). The aliphatic nitroalkene reacted smoothly with 2-hydroxy-1,4-naphthoquinone under the present reaction conditions to give the product in high yield (entry 1). The C-alkylation of 2-hydroxy-1,4-naphthoquinone was controlled by the electronic factors of the β-nitrostyrenes. The reaction time varied according to the nature of the substituent on the β-nitrostyrene. For example, the conjugate addition of 2-hydroxy-1,4-naphthoquinone with β-nitrostyrene containing electron-donating groups (OMe and Me) required longer reaction times for the completion of the reaction (entries 3–5). However, nitroolefins bearing electron-withdrawing groups (Cl, Br, CF_3, and NO_2) required relatively shorter reaction times to furnish the Michael adducts in good yields (entries 6–9). Acid-sensitive furan and thiophene moieties survived under the present reaction conditions. Interestingly, the reaction conditions are equally efficient for the sterically hindered substrates such as 1-(2-nitrovinyl) naphthalene and 3-(2-nitrovinyl)-1-phenyl-1*H*-indole to afford their corresponding alkylated product in good yields (entries 12 and 13). All the products obtained were characterized by ^{1}H NMR, ^{13}C NMR, LC–MS, and HRMS.

Further, the structure of the representative compound **3i** was confirmed by single crystal X-RD analysis shown in Figure 1.

It was reported earlier that the product (**3n**) furnished by the reaction of 2-hydroxynaphthoquinone (**1**) with 1-nitrocyclohexene (**2n**) served as the precursor compound of 5*H*-benzo[*b*]carbazole-6,11-dione, which exhibited antineoplastic activity.[12] Hence, under

Table 2
The C-alkylation of 2-hydroxy-1,4-naphthoquinone with nitroolefins



Entry	R	Product[16,17]	Time (h)	Yield[a,b] (%)
1		**3a**	10	90
2		**3b**	12	85
3		**3c**	16	88
4		**3d**	12	90
5		**3e**	12	90
6		**3f**	10	82
7		**3g**	10	85
8		**3h**	10	86
9		**3i**	8	86
10		**3j**	20	84
11		**3k**	18	88
12		**3l**	12	85
13		**3m**	12	80

[a] All the reactions were conducted in 3 mmol scale.
[b] Isolated yields.

the present reaction conditions, we obtained the trans diastereomer as the sole product (precursor compound) in good yield (Scheme 1). The trans isomer was confirmed by NOE studies. No NOE enhancement was observed by saturation of either of the protons H3 or H2, which showed that H3 and H2 are aligned in trans orientation. The relative configuration of the product can be assigned as $2S^*3R^*$.

We assume that the water may act as amphiphilic dual catalyst in this reaction.[2g] (Scheme 2). Hence, we speculate that water may activate the nitro group of β-nitrostyrene and the hydroxyl group of 2-hydroxynaphthoquinone through hydrogen bonding. This facilitates the addition of 2-hydroxynaphthoquinone to the β-nitrostyrene to form the intermediate (**A**) which upon losing the proton gives the adduct (**B**). The adduct (**B**) abstracts the proton either from water or from 2-hydroxynaphthoquinone to afford *aci*-nitro compound (**C**). This *aci*-nitro compound tautomerizes to furnish the nitro alkylated product.

Further to examine our speculation, we conducted the reaction of 1-methyl-4-(2-nitrovinyl)benzene (**2e**) with 2-hydroxynaphthoquinone in D_2O (Scheme 3). We were able to obtain only the deuterated product which can be detected from the crude ^{1}H NMR and

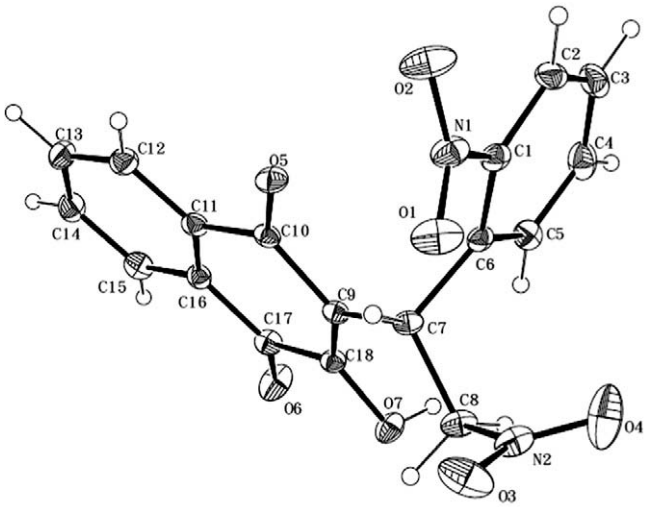
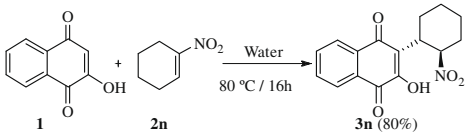
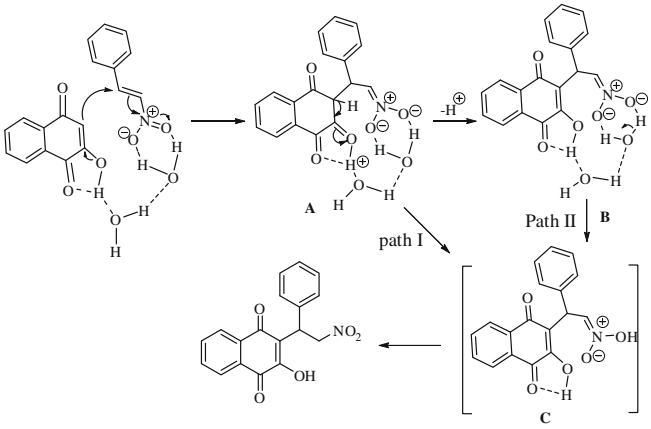


Figure 1. X-ray crystal structure of **3i** (ORTEP view).[15]

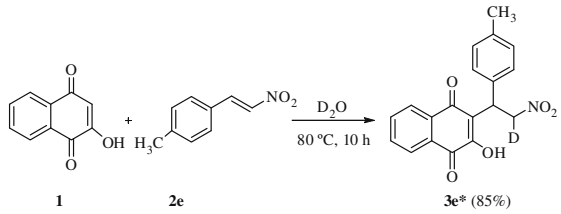


Scheme 1. Reaction of 2-hydroxy-1,4-naphthoquinone with 1-nitrocyclohexene.



Scheme 2. Plausible mechanism for the formation of nitroalkylated 2-hydroxynaphthoquinone.

^{13}C NMR spectrum (Table 3). Spectral comparison of deuterated product (**3e***) and undeuterated product **(3e)** can be seen from



Scheme 3. Reaction of 2-hydroxynaphthoquinone and 1-methyl-4-(2-nitrovinyl)benzene (**2e**) in D_2O.

Table 3
Comparison of ^{1}H NMR and ^{13}C NMR spectra of compounds **3e** and **3e***

		Compound 3e	Compound 3e*
^{1}H Spectrum	C_2	5.43 (dd, J = 13.2, 9.0 Hz, 1H) 5.29 (dd, J = 9.0, 6.4 Hz, 1H)	5.25 (d, J = 6.8 Hz, 1H)
	C_3	5.09 (dd, J = 13.2, 6.4 Hz, 1H)	5.09 (d, J = 6.8 Hz, 1H)
^{13}C Spectrum	C_2	77.3	76.7 (t, J = 23.0 Hz)
	C_3	38.7	38.2

the Table 3. D_2O experiment supports that this reaction follows path II mechanism as shown in Scheme 2.

This method is also amenable for the large-scale reactions. In this context, we performed the reaction of 2-hydroxynapthoquinone (50 mmol) with 1-methyl-4-(2-nitrovinyl) benzene (**2e**) (60 mmol) in 50 mL of water under the present conditions and we obtained the product (**3e**) in high yield (85%).

In summary, we have developed an efficient and catalyst-free C-alkylation of 2-hydroxy-1,4-naphthoquinones to nitroalkenes employing 'on water' conditions to afford 2-hydroxy-3-functionalized naphthoquinones in good yields. Simple reaction conditions, catalyst-free and easy isolation of the compounds are the attractive features of this methodology. Moreover, this protocol was also proved to be efficient on a multigram scale, which will be applicable for industrial processes.

Acknowledgment

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.06.107.

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15. CCDC number of the **3i** is 720909. These data can be obtained free of charge from Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/datarequest/cif.
16. *General procedure for the C-alkylation of 2-hydroxy-1,4-naphthoquinones*: A mixture of 2-hydroxy-1,4-naphthoquinone (**1**) (3 mmol) and β-nitrostyrene (**2**) (3.6 mmol) was suspended in 5 mL of water, and the reaction mixture was heated at 80 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, solid product obtained was filtered and washed with water (2 × 10 mL) and *n*-hexane (3 × 10 mL). Then the solid was dried under vacuum to obtain the product (**3**) in almost pure form. In case of liquid compounds, the crude reaction mixture was diluted with EtOAc (50 mL) and washed with water (3 × 10 mL). The organic layer was dried over anhydrous $MgSO_4$, followed by evaporation of the solvent to obtain the crude product, which was passed through a small plug of silica gel to obtain the pure product (**3**).
17. *Spectral data: 2-hydroxy-3-(4-methyl-1-nitropentan-2-yl)naphthalene-1,4-dione* (**3a**). Light brown solid; mp: 80–82 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.48 (br s, 1H), 7.99 (d, J = 7.4 Hz, 2H), 7.87–7.78 (m, 2H), 4.92 (dd, J = 12.3, 9.2 Hz, 1H), 4.75 (dd, J = 12.3, 6.0 Hz, 1H), 4.04–3.96 (m, 1H), 1.46–1.38 (m, 2H), 1.36–1.29 (m, 1H), 0.86 (d, J = 6.4 Hz, 3H), 0.82 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 183.9, 180.7, 156.8, 134.7, 133.3, 131.9, 129.8, 126.0, 125.7, 120.7, 77.7, 38.7, 32.1, 25.5, 23.2, 21.7. MS (ESI) (m/z) (relative intensity) 303 (M^+, 24), 256 (35), 241 (50), 231 (100), 200 (97), 187 (38). HRMS (ESI) calcd for $C_{16}H_{17}NO_5Na$ $(M+Na)^+$ 326.1015, found: 326.1004. *2-Hydroxy-3-(2-nitro-1-phenylethyl)naphthalene-1,4-dione* (**3b**). Yellow solid; m.p.: 154–156 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.50 (br s, 1H), 7.94–7.92 (m, 2H), 7.77–7.71 (m, 2H), 7.40 (d, J = 6.9 Hz, 2H), 7.30 (t, J = 6.8 Hz, 2H), 7.21 (d, J = 6.7 Hz, 1H), 5.47 (dd, J = 13.2, 8.7 Hz, 1H), 5.31 (dd, J = 8.7, 6.9 Hz, 1H), 5.16 (dd, J = 13.2, 6.9 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 183.8, 180.9, 156.4, 138.5, 134.8, 133.3, 131.7, 129.8, 128.6, 127.9, 127.1, 126.0, 125.8, 120.8, 76.7, 38.6. MS (ESI) (m/z) (relative intensity) 323 (M^+, 13), 322 (100), 275 (77). HRMS (ESI) calcd for $C_{18}H_{13}NO_5Na$ $(M+Na)^+$ 346.0713, found: 346.0691.