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Catalyst-free Friedel–Crafts alkylation of naphthols with nitrostyrenes in the presence of water

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ABSTRACT

Accelerated Michael-type Friedel–Crafts alkylation of naphthols with nitrostyrenes in the presence of water is reported. The procedure is simple, catalyst-free, and affords good yields of the products.

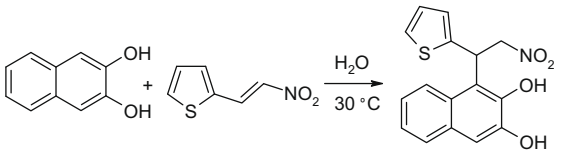
The environment calls on the entire research community to define long-term strategic goals for clean chemistry and to reduce pollutants, especially organic solvents, whose recovery is mandated by evermore strict laws. To reduce the use of ecologically hazardous chemicals, it is advantageous to carry out organic reactions in aqueous media. Indeed, water is recognized as an attractive medium for many organic reactions. Reactions in aqueous media are more environmentally safe, simple to handle, cheaper to operate, and are especially important in industry.[1,2]

The Friedel–Crafts alkylation is a very important process for C–C bond formation in organic chemistry.[3] Various aromatic compounds, including benzenes with electron-donating substituents, furans, pyrroles, and indoles, have been applied successfully in a number of Friedel–Crafts reactions with diverse electrophiles. Enantioselective variants of this reaction have also been studied in the presence of chiral metal complexes.[4,5] Nevertheless, most reports in this area are focused on relatively more reactive indole or pyrrole derivatives.[6] There are only a few reports on the Friedel–Crafts reaction of benzene derivatives bearing highly electron-donating groups.[4e] Hence, there is a need to develop novel Friedel–Crafts reactions, especially for electron-rich arenes. Naphthols have been demonstrated to be good donors in Friedel–Crafts alkylations with a range of electrophiles, and various biologically active compounds and useful chiral ligands for asymmetric catalysis can be prepared easily by this method.[7,8] Although Friedel–Crafts alkylations of naphthol derivatives with activated species such as iminium ions,[9] α,β-unsaturated olefins[8a], and aza-dicarboxylate[7b] are well studied, there is only one report on the reaction of 2-naphthol and nitroolefins in the literature.[10]

In continuation of our studies using water as catalyst or solvent for organic transformations, and encouraged by our results using water for Michael addition of amines and thiols to activated olefins,[11] and ring-opening of epoxides by amines in water,[12] we envisioned that the Friedel–Crafts reaction between a nitrostyrene and a 2,3-dihydroxy-naphthalene would be possible through activation of the nitro group in the nitrostyrene and hydroxy groups in 2,3-dihydroxynaphthalene through hydrogen bonding in aqueous medium, Scheme 1.

A range of organic solvents were screened for the Friedel–Crafts reaction of 2,3-dihydroxynaphthalene and 2-(2-nitrovinyl)thiophene.[13] As shown in Table 1, we found that the best yield was obtained in the presence of water. After optimization of the solvent, we studied the reaction at different temperatures, and found out that the best yield was obtained at 30 °C.

Having established the optimal reaction conditions, we next expanded our study to other naphthols such as 2-naphthol **2** and 2,7-dihydroxynaphthalene **3**. As shown in Table 2, 2,3-dihydroxynaphthalene and 2,7-dihydroxynaphthalene showed very good reactivity towards 2-(2-nitrovinyl)-thiophene in the presence of water, and good to excellent yields of products were obtained. However, 2-naphthol gave only a moderate yield. Also, electron-donating and electron-withdrawing groups on the phenyl ring of the nitrostyrene decreased the yield of the reaction. Reaction of 1-naphthol with nitrostyrene gave low yields of the Friedel–Crafts products (ca. less than 10%). We did not observe O-alkylation products in these reactions, and only C-alkylation products were obtained in all cases. Work-up was very simple, involving filtration of the solid material or decanting the water. Purification was accomplished by washing with hot petroleum ether or by using



Scheme 1. Reaction of 2,3-dihydroxynaphthalene with 2-(2-nitrovinyl)thiophene in the presence of water.

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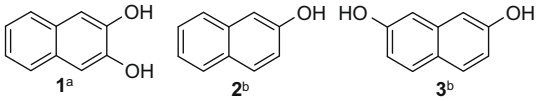
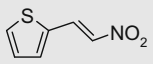
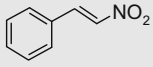
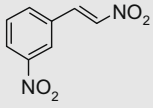
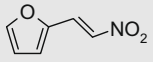
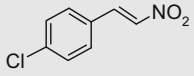
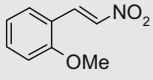
Table 1
Friedel–Crafts alkylation of 2,3-dihydroxy-naphthalene with 2-(2-nitrovinyl)thiophene in different solvents

Entry	Solvent	Yield[a] (%)
1	H_2O	92
2	C_2H_5OH	30
3	CH_3OH	38
4	CH_3CN	60
5	$CHCl_3$	52
6	THF	14
7	DMSO	50

[a] Yields based on 2-(2-nitrovinyl)thiophene.

Table 2
Catalyst-free Friedel–Crafts alkylation of naphthol **1**, **2** or **3** with 2-(2-nitrovinyl)thiophene, nitrostyrenes and 2-(2-nitrovinyl)furan in the presence of water at 30 °C



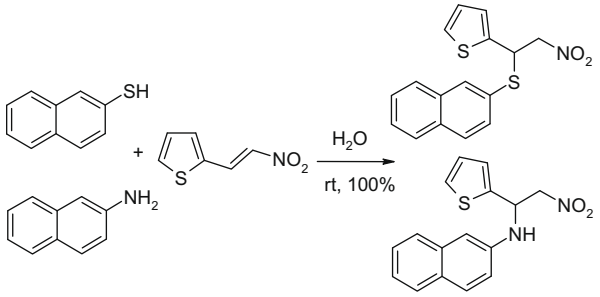
Entry		Naphthol	Yield[c] (%)
1		**1**	92
2		**2**	57
3		**3**	75
4		**1**	87
5		**2**	55
6		**3**	60
7		**1**	50
8		**2**	45
9		**1**	93
10		**2**	55
11		**3**	80
12		**1**	75
13		**2**	40
14		**3**	33
15		**2**	40

[a] Reaction conditions: naphthol **1** (1 mmol), nitrostyrene (1.1 mmol).
[b] Reaction conditions: naphthol **2** or **3** (1.1 mmol), nitrostyrene (1 mmol).
[c] Isolated yields.

column chromatography (silica gel, ethyl acetate: petroleum ether). Reaction of 2-naphthalenethiol and 2-amino- naphthalene with 2-(2-nitrovinyl)thiophene gave the corresponding thia and aza-Michael addition products in 100% yields, Scheme 2.

Theoretical calculations to determine the optimized parameters (dipole moment, solvation energy, and partial charge on the α-position) of 2,3-dihydroxynaphthalene were performed with the HF/6-311G** basis set using Gaussian software. As shown in Table 3, the dipole moment and the partial charge on the α-position of 2,3-dihydroxynaphthalene in water are greater than in organic solvents, which may ascribe the higher nucleophilic ability of the α-carbon in 2,3-dihydroxy-naphthalene toward electrophiles.

In conclusion, we have reported a very mild, simple, and catalyst-free method for the Friedel–Crafts alkylation of naphthols in aqueous medium. The yields are good to excellent, and the work-up is very simple especially on large scale.



Scheme 2. Reaction of 2-naphthalenethiol and 2-amino-naphthalene with 2-(2-nitrovinyl)thiophene in the presence of water.

Table 3
Calculated parameters for 2,3-dihydroxynaphthalene in different solvents using the HF/6-311G** basis set

Solvent	μ (Debye)[a]	δ[b]	ΔG#[c]
H_2O	3.7116	−0.116498	−11.63
Gas phase	2.6349	−0.085354	—
C_2H_5OH	3.6459	−0.115057	−11.26
CH3OH	3.6702	−0.115678	−14.29
CHCl3	3.1458	−0.092739	−3.75
Toluene	2.9555	−0.089616	−2.95
CH_3CN	3.3577	−0.095791	−2.13
DMSO	3.3669	−0.095831	−5.95
Acetone	3.3282	−0.095397	−6.27
THF	3.2263	−0.093837	−4.57
CH_3NO_2	3.3595	−0.095824	−5.07

[a] Dipole moment for 2,3-dihydroxynaphthalene in different solvents.
[b] Partial charge on C-1 of 2,3-dihydroxynaphthalene.
[c] Solvation energy.

Acknowledgments

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13. *General procedure for the reaction of naphthol derivatives with nitrostyrene*: In a round-bottomed flask equipped with a magnetic stirrer, naphthol, nitrostyrene (as noted in Table 2), and water (3 mL) were added. The mixture was stirred at room temperature, and the progress of the reaction was monitored by TLC (silica gel, ethyl acetate: petroleum ether 1:3). After completion of the reaction (8 h), the products were extracted with ethyl acetate (2 ×10 mL). Evaporation of the solvent gave a crude product. Purification was accomplished by washing with hot petroleum ether (Table 2, entries 1, 4, 9, and 12) or using column chromatography (silica gel, ethyl acetate: petroleum ether 1:3).
Selected spectroscopic data: Table 2, entry 1: IR (KBr): ν = 3422, 1638, 1549, 1377, 1259, 1184, 1008 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$/DMSO), δ, 5.20–5.30 (m, 2H), 5.71 (t, J = 7.4 Hz, 1H), 6.66 (dd, J = 4.9, 3.6 Hz, 1H), 6.81 (d, J = 3.3 Hz, 1H), 6.90 (d, J = 5.1 Hz, 1H), 6.97 (s, 1H), 7.04–7.11 (m, 2H), 7.37 (d, J = 8.0 Hz, 1H), 7.60 (br, 1H, –OH), 7.73 (d, J = 8.4 Hz, 1H), 9.85 (br s, 1H, –OH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$/DMSO), δ, 37.2, 78.9, 109.9, 116.8, 121.8, 123.2, 123.9, 124.3, 125.0, 126.6, 126.9, 127.2, 129.4, 142.5, 145.5, 145.7 ppm.Decomposed at 130 °C. Anal. Calcd for $C_{16}H_{13}NO_4S$: C, 60.95; H, 4.12; N, 4.44. Found: C, 60.40; H, 3.90; N, 4.54.
Table 2, entry 3: ^1H NMR (500 MHz, $CDCl_3$/DMSO), δ, 4.85 (dd, J = 13.0 Hz, 6.7, 1H) 4.96 (dd, J = 12.9, 7.7 Hz, 1H), 5.29 (t, J = 7.3 Hz, 1H), 6.35 (m, 2H), 6.44 (d, J = 8.8 Hz, 1H), 6.51 (d, J = 3.2 Hz, 1H), 6.61 (d, J = 5.1 Hz, 1H), 6.82 (s, 1H), 6.99 (d, J = 8.7 Hz, 1H), 7.03 (d, J = 8.7 Hz, 1H), 8.99 (br s, 1H, OH), 9.36 (br s, 1H, OH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$/DMSO), δ, 29.5, 79.2, 104.3, 114.7, 115.2, 115.4, 123.4, 124.3, 125.0, 125.5, 129.4, 130.3, 134.5, 143.5, 153.8, 156.5 ppm.
Table 2, entry 4: IR (KBr): ν = 3440, 1632, 1547, 1516, 1458, 1366, 1259, 1180, 1012 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$/DMSO): δ = 5.28–5.34 (m, 2H), 5.58 (t, J = 7.5 Hz, 1H), 7.01–7.16 (m, 6H), 7.25–7.31 (m, 3H), 7.42 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 8.5 Hz, 1H), 9.81 (br s, 1H, –OH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$/DMSO), δ, 41.9, 78.5, 110.0, 117.7, 122.5, 123.6, 124.2, 127.2, 127.3, 128.0, 128.2, 128.9, 129.9, 140.7, 145.8, 146.2 ppm. Decomposed at 150 °C. Anal. Calcd for $C_{18}H_{15}NO_4$: C, 69.90; H, 4.85; N, 4.53. Found: C, 69.45; H, 4.66; N, 4.58.
Table 2, entry 6: ^1H NMR (500 MHz, $CDCl_3$/DMSO), δ, 5.08–5.23 (m, 3H), 6.55–6.65 (m, 2H), 6.9 (m, 3H), 7.10–7.23 (m, 5H), 8.99 (br s, 1H), 9.17 (br s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$/DMSO), δ, 40.3, 79.2, 104.9, 115.3, 115.6, 115.8, 123.7, 126.8, 128.0, 128.5, 129.3, 130.4, 135.1, 140.7, 155.7, 156.5 ppm.
Table 2, entry 9: IR (KBr): ν = 3515, 3412, 1635, 1551, 1379, 1280, 1182, 1015 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$/DMSO), δ, 4.96 (dd, J = 13.2, 6.9 Hz, 1H), 5.21 (dd, J = 13.2, 7.6 Hz, 1H), 5.62 (t, J = 7.1 Hz, 1H), 5.79 (d, J = 2.7 Hz, 1H), 6.0 (t, J = 7.2 Hz, 1H), 6.92 (s, 1H), 6.96–7.03 (m, 2H), 7.05 (s, 1H), 7.31 (d, J = 7.9 Hz, 1H), 7.58 (d, J = 8.3 Hz, 1H), 7.7 (br s, 1H, OH), 9.81 (br s, 1H, OH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$/DMSO), δ, 35.9, 77.0, 106.9, 110.3, 111.1, 115.2, 122.5, 123.5, 124.1, 127.3, 127.9, 129.8, 141.8, 146.2, 146.3, 153.5 ppm. Decomposed at 172 °C. Anal. Calcd For $C_{16}H_{13}NO_5$: C, 64.21; H, 4.35; N, 4.68. Found: C, 63.98; H, 3.90; N, 4.54.
Table 2, entry 11: ^1H NMR (500 MHz, $CDCl_3$/DMSO): δ = 5.0 (dd, J = 13.3, 6.9 Hz, 1H), 5.40 (dd, J = 13.2, 8.1 Hz, 1H), 5.75 (t, J = 7.3 Hz, 1H), 5.93 (d, J = 3.1 Hz, 1H), 6.14 (t, J = 2.42 Hz, 1H), 6.80–6.85 (m, 3H), 6.9 (s, 1H), 6.95 (s, 1H), 7.41 (d, J = 8.7 Hz, 1H), 7.46 (d, J = 8.7 Hz, 1H), 9.3 (br s, 1H, OH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$/DMSO), δ, 35.6, 76.9, 104.6, 106.5, 110.7, 112.6, 115.4, 115.5, 123.6, 129.5, 130.5, 134.9, 141.2, 153.5, 154.3, 156.3 ppm.
Table 2, entry 14: ^1H NMR (500 MHz, $CDCl_3$/DMSO), δ, 5.14 (dd, J = 12.9, 7.0 Hz, 1H), 5.16–5.36 (m, 2H), 6.50–6.80 (m, 2H), 7.03 (d, J = 7.7, 2.3 Hz, 2H), 7.24 (m, 3H), 7.34 (d, J = 8.7 Hz, 1H), 7.40 (d, J = 8.7 Hz, 1H), 9.0 (br s, 1H, OH), 9.2 (br s, 1H, OH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$/DMSO), δ, 40.5, 79.1, 104.9, 115.2, 115.5, 115.8, 123.9, 128.7, 129.4, 129.6, 130.6, 132.5, 135.0, 139.5, 154.0, 156.7 ppm.