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# Friedel–Crafts alkylation of *N*,*N*-dialkylanilines with nitroalkenes catalyzed by heteropolyphosphotungstic acid in water

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ABSTRACT

Michael-type Friedel–Crafts alkylation of *N*,*N*-dialkylanilines with nitroalkenes catalyzed by heteropolyphosphotungstic acid (HPW) is investigated in water. The reaction is simple, clean, and affords good to excellent yields of products using small quantity of catalyst. Also, theoretical study on the nature of reaction in water is reported.



## 1. Introduction

Heteropoly acids (HPAs) are used as homogeneous and heterogeneous acid due to their strong acidity, selectivity and safety in handling in comparison to the conventional mineral acids. They are also used as catalyst in oxidation reactions and have the potential of great economic rewards and green benefits [1]. Heteropolyphosphotungstic acid (HPW), the strongest HPA in the Keggin series, is the common catalyst of choice because of its high acidic strength, relatively high thermal stability, and lower oxidation potential compared with molybdenum HPAs [2]. Recently, heteropolyphosphotungstic acid has been used as efficient catalyst in several reactions such as esterification [3], etherification [4], Friedel–Crafts alkylation and acylation [5], isomerization [6], hydrolysis [7], Michael addition [8], protection of carbonyl compounds and alcohols [9], oxidation [10], and etc. [11]. In addition, Saidi and co-worker have used HPW as efficient catalyst for epoxide ring opening [12], Mannich reaction [13] and Friedel–Crafts alkylation of indoles and pyrroles in water [14]. Therefore, using a very small amount of HPW in water will be an ideal methodology, providing that the HPW shows higher catalytic activity under these conditions.

The Friedel–Crafts alkylation is an interesting reaction for C—C bond formation in organic chemistry. Arene derivatives such as substituted anilines, phenols, naphthols and heteroarenes such as indole, dihydroindole and pyrrole derivatives have been successfully used as nucleophiles in Friedel–Crafts reaction in order to obtain arene's derivatives [15]. On the other hand, unsaturated electrophiles such as enals, enones, chalcones, nitroalkenes, β,γ-unsaturated α-ketoesters, and α,α-dicyanoolefins have been applied extensively in Friedel–Crafts alkylation [16]. Nevertheless, most reports in this area are focused on relatively more reactive indole or pyrrole derivatives. There are only a few reports on the Friedel–Crafts reaction of *N*,*N*-dialkylaniline derivatives with unsaturated carbonyl compounds [17]. Friedel–Crafts alkylation of *N*,*N*-dialkylanilines with nitroolefins is rare. The only report in this area is the Friedel–Crafts alkylation of 3-methoxy-*N*,*N*-dimethylaniline with nitrostyrene, which have been reported by Takenaka et al. using 7-azaindoliumtetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) as catalyst (Scheme 1) [18]. To the best of our knowledge, there is not any other report on the Friedel–Crafts alkylation of *N*,*N*-dialkylanilines with nitroalkenes in the literature. So, there is a need to develop a novel Friedel–Craft reaction, especially for the electron-rich arenes.

The use of nitroalkenes as electrophiles has attracted significant interest in recent years. The activating effect of nitro group, as well as the ease of transforming to other functional groups, makes these compounds as suitable building blocks for the synthesis of many interesting pharmaceutical compounds [19].

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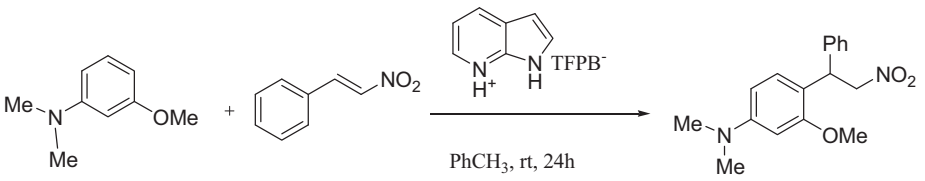



**Scheme 1.** Previous report on Friedel–Crafts alkylation of *N*,*N*-dialkylanilines.

## 2. Experimental

### 2.1. Reagents and equipments

All chemicals were purchased from commercial sources and used as received. Tap water was used in all experiments. Solvents were used as received without further purifications and drying.

Melting points were determined with a Branstead Electrothermal 9200 apparatus and are uncorrected. $^1$H NMR and $^{13}$C NMR spectra were determined with a Brucker AMX 300 spectrometer in $CDCl_3$ with TMS as internal standard. Elemental analyses were conducted with a Perkin-Elmer 2004 (II) CHN analyzer.

### 2.2. Reaction of N,N-dialkylanilines with nitroalkenes: general procedure

In a test tube equipped with a magnetic stirrer, *N*,*N*-dialkylaniline (2.2 mmol), nitroalkene (2 mmol), and water (5 mL) were added. To this mixture, HPW (0.1 g, 0.035 mmol, 0.0175 mol%) was added and stirred at reflux temperature. Progress of the reaction was monitored by TLC. After completion of the reaction (18 h), the products were collected by filtration or extraction with ethyl acetate (2 × 10 mL, in the case of oily products). Purification was accomplished using column chromatography (silica gel and gradient of petroleum ether–ethyl acetate). The products were characterized by their $^1$H and $^{13}$C NMR spectra and CHN analyses.

*N*,*N*-dimethyl-4-(2-nitro-1-phenylethyl)benzenamine (Table 2, entry 1). Yield: 0.481 g (89%); viscous yellow oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 3.02 (6H, s), 4.85–4.99 (3H, m), 6.60 (2H, d, $J$ = 8.6 Hz), 7.10 (2H, d, $J$ = 8.7 Hz), 7.22–7.37 (5H, m). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 42.6, 48.2, 79.2, 112.1, 126.0, 127.5, 127.6, 128.5, 128.8, 139.5, 146.5. Anal. Calcd. (%) for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.12; H, 6.51; N, 10.13.

*N*,*N*-diethyl-4-(2-nitro-1-phenylethyl)benzenamine (Table 2, entry 2). Yield: 0.554 g (93%); viscous yellow oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.22 (6H, t, $J$ = 7.1 Hz), 3.41 (4H, q, $J$ = 7.2 Hz), 4.87–5.02 (3H, m), 6.70 (2H, d, $J$ = 8.6 Hz), 7.15 (2H, d, $J$ = 8.6), 7.28–7.47 (5H, m). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 12.3, 44.0, 48.0, 79.4, 111.5, 125.2, 127.4, 127.7, 128.3, 128.6, 139.9, 146.8. Anal. Calcd. (%) for $C_{18}H_{22}N_2O_2$: C, 72.46; H, 7.43; N, 9.39. Found: C, 72.69; H, 7.58; N, 9.71.

*N*,*N*-dimethyl-4-(1-(naphthalen-3-yl)-2-nitroethyl)benzenamine (Table 2, entry 4). Yield: 0.576 g (90%); yellow viscous oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 2.95 (6H, s), 5.04–5.13 (2H, m), 5.69 (1H, t, $J$ = 8.1 Hz), 6.67 (2H, d, $J$ = 8.4 Hz), 7.17 (2H, d, $J$ = 8.4 Hz), 7.38–7.55 (4H, m), 7.81–7.90 (2H, m), 8.16 (1H, d, $J$ = 8.2 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 40.4, 43.8, 79.4, 112.7, 123.2, 123.8, 125.2, 125.8, 126.2, 126.6, 128.2, 128.6, 128.9, 131.2, 134.2, 135.3, 149.8. Anal. Calcd. (%) for $C_{20}H_{20}N_2O_2$: C, 74.98; H, 6.29; N, 8.74. Found: C, 74.68; H, 6.58; N, 8.95.

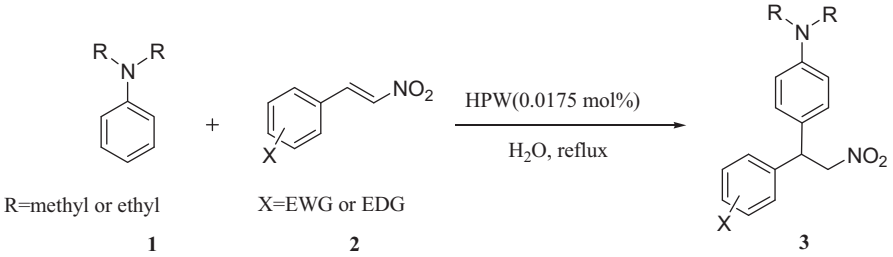
*N*,*N*-diethyl-4-(1-(naphthalen-7-yl)-2-nitroethyl)benzenamine (Table 2, entry 5). Yield: 0.660 g (85%); viscous yellow oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.11 (6H, t, $J$ = 7.0 Hz), 3.27 (4H, q, $J$ = 7.0 Hz), 4.98–5.13 (2H, m), 5.60 (1H, t, $J$ = 8.2 Hz), 6.56(2H, d, $J$ = 8.8 Hz), 7.08 (2H, d, $J$ = 8.8 Hz), 7.38–7.49 (4H, m), 7.76 (1H, d, $J$ = 8.1 Hz), 7.83 (1H, d, $J$ = 8.1 Hz), 8.13 (1H, d, $J$ = 8.1 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 12.5, 43.8, 44.2, 79.4, 111.8, 123.2, 123.8, 125.2, 125.8, 126.6, 128.1 (2C), 128.8, 128.9, 131.2, 134.2, 135.7, 149.7. Anal. Calcd. (%) for $C_{22}H_{24}N_2O_2$: C, 75.81; H, 6.94; N, 8.04. Found: C, 75.83; H, 7.20; N, 8.04.

4-(1-(2-chlorophenyl)-2-nitroethyl)-*N*,*N*-dimethylbenzenamine (Table 2, entry 6). Yield: 0.53 g (87%); yellowish solid; mp 93–95 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 2.95 (6H, s), 4.89–5.02 (2H, m), 5.35 (1H, t, $J$ = 8.1 Hz), 6.66 (2H, d, $J$ = 8.8 Hz), 7.11 (2H, d, $J$ = 8.8 Hz), 7.19–7.41 (4H, m). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 40.4, 44.4, 78.1, 112.6, 124.8, 127.1, 128.0, 128.5, 128.7, 130.3, 134.1, 137.3, 149.8. Anal. Calcd. (%) for $C_{16}H_{17}ClN_2O_2$: C, 63.05; H, 5.62; N, 9.19. Found: C, 63.12; H, 5.51; N, 9.03.

4-(1-(2-chlorophenyl)-2-nitroethyl)-*N*,*N*-diethylbenzenamine (Table 2, entry 7). Yield: 0.564 g (85%); viscous yellow oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.24 (6H, t, $J$ = 7.0 Hz), 3.35 (4H, q, $J$ = 7.1 Hz), 5.00 (2H, m), 5.45 (1H, t, $J$ = 8.1 Hz), 6.65 (2H, d, $J$ = 8.6 Hz), 7.11–7.73 (6H, m). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 44.6, 47.4, 77.6, 112.4, 123.5, 127.5, 127.8, 129.4, 129.8, 130.6, 134.1, 137.4, 149.8. Anal. Calcd. (%) for $C_{18}H_{21}ClN_2O_2$: C, 64.96; H, 6.36; N, 8.42. Found: C, 65.12; H, 6.55; N, 8.33.

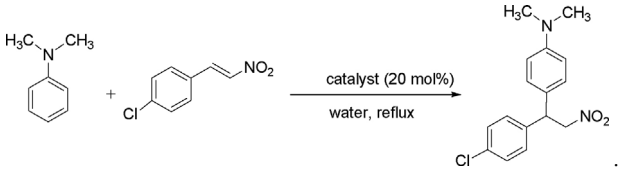
4-(1-(4-chlorophenyl)-2-nitroethyl)-*N*,*N*-dimethylbenzenamine (Table 2, entry 8). Yield: 0.561 g (92%); white solid; mp 62–65 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 2.94 (6H, s), 4.77–4.95 (3H, m), 67 (2H, dd, $J$ = 6.8 and 1.9 Hz), 7.06 (2H, dd, $J$ = 6.8 and 1.9 Hz), 7.18–7.32 (4H, m). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 40.4, 47.6, 79.4, 112.8, 126.1, 128.3, 129.0, 129.1, 133.1, 138.7, 149.9. Anal. Calcd. (%) for $C_{16}H_{17}ClN_2O_2$: C, 63.05; H, 5.62; N, 9.19. Found: C, 63.59; H, 5.78; N, 8.90.

4-(1-(4-methoxyphenyl)-2-nitroethyl)-*N*,*N*-dimethylbenzenamine (Table 2, entry 9). Yield: 0.498 g (83%); viscous yellow oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 2.95 (6H, s),




**Scheme 2.** Friedel–Crafts alkylation of *N*,*N*-dialkylanilines with nitroalkenes.

**Table 1**
Reaction of *N*,*N*-dimethyaniline with 4-chloro nitrostyrene in the presence of different water-tolerant catalyst




| Catalyst | HPW[a] | PTSA | $FeCl_3{\cdot}6H_2O$ | $H_3BO_3$ | CuCl | β-CD | $ZrOCl_2{\cdot}8H_2O$ | $SnCl_2$ | $CuCl_2$ | $NiCl_2{\cdot}6H_2O$ | $SiO_2$–$SO_3H$[b] | DABCO |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Yield (%) | 92 | 50 | 50 | 35 | 30 | 33 | 25 | 20 | Trace | 10 | Trace | Trace |

[a] 0.0175 mol% of HPW was used.
[b] The reaction was carried out with 0.2 g of $SiO_2$–$SO_3H$ in toluene.

3.81 (3H, s), 4.81–4.96 (3H, m), 6.70 (2H, d, *J* = 8.7 Hz), 6.87 (2H, d, *J* = 8.7 Hz), 7.10 (2H, d, *J* = 8.7 Hz), 7.18 (2H, d, *J* = 8.6 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 40.5, 47.5, 55.2, 79.8, 112.7, 114.2, 128.2, 128.6, 129.8, 132.0, 149.7, 158.6. Anal. Calcd. (%) for $C_{17}H_{20}N_2O_3$: C, 67.98; H, 6.71; N, 9.33. Found: C, 67.75; H, 6.88; N, 9.43.

*N*,*N*-diethyl-4-(1-(4-methoxyphenyl)-2-nitroethyl)benzenamine (Table 2, entry 10). Yield: 0.591 g (90%); viscous yellow oil. $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.17 (6H, t, *J* = 7.0 Hz), 3.34 (4H, q, *J* = 7.1 Hz), 3.83 (3H, s), 4.78 (1H, t, *J* = 7.7 Hz), 4.92–4.96 (2H, m), 6.63 (2H, d, *J* = 8.5 Hz), 6.87 (2H, d, *J* = 8.7), 7.06 (2H, d, *J* = 8.7 Hz), 7.19 (2H, d, *J* = 8.6 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 12.5, 44.3, 47.5, 55.2, 79.9, 111.9, 114.2, 128.4, 128.6, 149.5, 158.6, two quaternary carbons were not observed. Anal. Calcd. (%) for $C_{19}H_{24}N_2O_3$: C, 69.49; H, 7.37; N, 8.53. Found: C, 69.69; H, 7.68; N, 8.70.

*N*,*N*-dimethyl-4-(2-nitro-1-(thiophen-2-yl)ethyl)benzenamine (Table 2, entry 11). Yield: 0.58 g (92%); viscous yellow oil. $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.92 (6H, s), 4.87–5.00 (3H, m), 6.66 (2H, d, *J* = 8.8 Hz), 6.88–6.95 (2H, m), 7.14–7.21 (3H, m). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 40.4, 43.9, 80.3, 112.6, 124.6, 124.9, 126.1, 126.9, 128.2, 143.6, 150.1. Anal. Calcd. (%) for $C_{14}H_{16}N_2O_2S$: C, 60.85; H, 5.84; N, 10.14. Found: C, 61.06; H, 5.60; N, 10.18.

*N*,*N*-diethyl-4-(2-nitro-1-(thiophen-2-yl)ethyl)benzenamine (Table 2, entry 12). Yield: 0.578 g (95%); viscous yellow oil. $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.19 (6H, t, *J* = 7.1 Hz), 3.37 (4H, q, *J* = 7.1 Hz), 4.87–5.07 (3H, m), 6.66 (2H, d, *J* = 8.8 Hz), 6.94–7.00 (2H, m), 7.15–7.26 (3H, m). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 12.5, 43.9, 44.2, 80.3, 111.7, 124.6, 124.76, 124.83, 126.8, 128.4, 143.7, 147.3. Anal. Calcd. (%) for $C_{16}H_{20}N_2O_2S$: C, 63.13; H, 6.62; N, 9.20. Found: C, 63.11; H, 6.95; N, 9.52.

4-(1-(2,4-dichlorophenyl)-2-nitroethyl)-*N*,*N*-dimethylbenzenamine (Table 2, entry 13). Yield: 0.576 g (85%); yellowish solid; mp 84–87 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.97 (6H, S), 4.87–5.02 (2H, m), 5.33 (1H, t, *J* = 8.2 Hz), 6.72 (2H, d, *J* = 8.8 Hz), 7.11 (2H, d, *J* = 8.8 Hz), 7.24–7.45 (3H, m). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 40.2, 43.9, 77.8, 112.1, 124.1, 127.4, 128.0, 128.5, 130.0, 133.6, 134.7, 135.9, 149.8. Anal. Calcd. (%) for $C_{16}H_{16}Cl_2N_2O_2$: C, 56.65; H, 4.75; N, 8.26. Found: C, 56.79; H, 4.97; N, 7.76.

4-(1-(2,4-dichlorophenyl)-2-nitroethyl)-*N*,*N*-diethylbenzenamine (Table 2, entry 14). Yield: 0.654 g (89%); viscous yellow oil. $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.18 (6H, t, *J* = 7.0 Hz), 3.35 (4H, q, *J* = 7.0 Hz), 4.87–5.02 (2H, m), 5.32 (1H, t, *J* = 8.2 Hz), 6.65 (2H, d, *J* = 8.8 Hz), 7.07 (2H, d, *J* = 8.8 Hz), 7.23–7.31 (2H, m), 7.45(1H, d, *J* = 1.6 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 12.5, 43.9, 44.2, 77.9, 111.7, 122.9, 127.4, 128.7, 128.8, 130.0, 133.6, 134.7, 136.1, 147.2. Anal. Calcd. (%) for $C_{18}H_{20}Cl_2N_2O_2$: C, 58.86; H, 5.49; N, 7.63. Found: C, 58.70; H, 5.0; N, 7.22.

*N*,*N*-diethyl-4-(2-nitro-1-*p*-tolylethyl)benzenamine (Table 2, entry 15). Yield: 0.580 g (93%); viscous yellow oil. $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.23 (6H, t, *J* = 7.0 Hz), 2.44 (3H, s), 3.41 (4H, q, *J* = 7.1 Hz), 4.85–5.00 (3H, m), 6.69 (2H, d, *J* = 8.6 Hz), 7.14 (2H, d, *J* = 8.6 Hz), 7.14 (2H, d, *J* = 8.5 Hz), 7.20–7.36 (4H, m). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 12.4, 20.8, 44.1, 47.7, 79.5, 111.7, 125.5, 127.3, 128.3, 129.1, 136.6, 136.9, 146.8. Anal. Calcd. (%) for $C_{19}H_{24}N_2O_2$: C, 73.05; H, 7.74; N, 8.97. Found: C, 72.69; H, 7.69; N, 8.78.

*N*,*N*-diethyl-4-(2-nitro-1-(2-nitrophenyl)ethyl)benzenamine (Table 2, entry 16). Yield: 0.597 g (87%); viscous yellow oil; $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.16 (6H, t, *J* = 7.0 Hz), 3.36 (4H, q, *J* = 7.1 Hz), 4.87–5.02 (3H, m), 6.62 (2H, d, *J* = 8.6 Hz), 7.01 (2H, d, *J* = 8.7 Hz), 7.50 (1H, t, *J* = 7.9 Hz), 7.60 (1H, d, *J* = 7.8 Hz), 8.04–8.14 (2H, m). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 12.5, 44.2, 47.8, 78.9, 111.9, 122.4, 122.5, 128.4, 129.8, 133.7, 135.8, 138.4, 147.2, 148.3. Anal. Calcd. (%) for $C_{18}H_{21}N_3O_4$: C, 62.96; H, 6.16; N, 12.24. Found: C, 63.13; H, 6.56; N, 12.43.

*N*,*N*-dimethyl-4-(2-nitro-1-(3-nitrophenyl)ethyl)benzenamine (Table 2, entry 17). Yield: 0.567 g (90%); viscous yellow oil; $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.94 (6H, s), 4.89–5.02 (3H, m), 6.67 (2H, d, *J* = 8.7 Hz), 7.06 (2H, d, *J* = 8.6 Hz), 7.48–7.59 (2H, m), 8.10 (1H, d, *J* = 8.4 Hz), 8.14 (1H, s). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 40.3, 47.8, 78.9, 112.8, 122.5, 128.2, 128.8, 129.9, 130.9, 133.7, 142.2, 146.9, 148.1. Anal. Calcd. (%) for $C_{16}H_{17}N_3O_4$: C, 60.94; H, 5.43; N, 13.33. Found: C, 61.12; H, 5.51; N, 13.09.

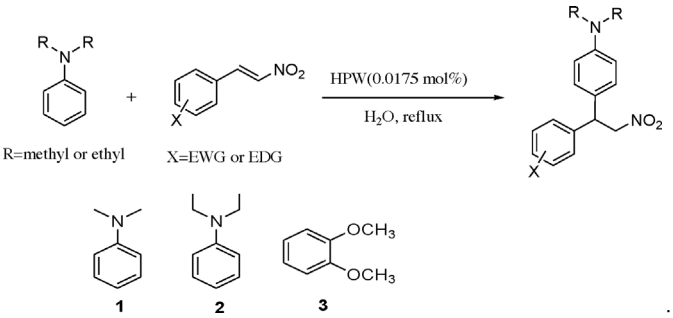
## 3. Results and discussion

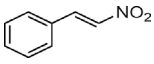
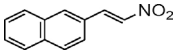
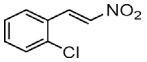
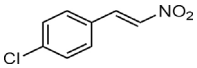
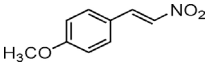
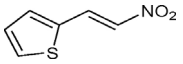
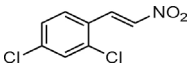
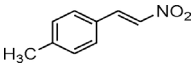
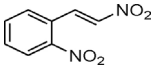
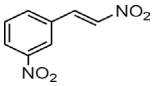
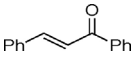
In continuation of our research toward the development of green organic chemistry by using water as the reaction medium or as catalyst [20], herein we report an efficient, novel, and green procedure for the Michael-type Friedel–Crafts alkylation of *N*,*N*-dialkylaniline with nitroolefins in water using small amount of HPW as catalyst as outlined in Scheme 2.

We initially examined the Friedel–Crafts alkylation of *N*,*N*-dimethylaniline with 4-chloro nitrostyrene at catalyst-free conditions in different solvents such as water, THF, diethyl ether, acetonitrile, hexane, dichloromethane, chloroform, methanol and ethanol in reflux temperature, with the exception of DMF, which was done at 100 °C. We have found that the best yield was obtained in water (40%) and no products were obtained in other used organic solvents. In continuation, we have focused our attempt to improve the reaction yield in water. Encouraged by the work of Saidi et al. [12–14] on using heteropoly acids in water as efficient homogenous catalyst, we have found that by using a small amount of heteropolyphosphotungstic acid in water at reflux temperature, good to excellent yield of product was obtained. Using HPW in organic solvents as heterogenous catalytic systems in reflux temperature gave only trace amount of product.

After successful results of using HPW in water, diversity of water-tolerant catalyst were also examined for the reaction of *N*,*N*-dimethylaniline with 4-chloro nitrostyrene in water and the

**Table 2**
Friedel–Crafts alkylation of nitroalkenes with *N*,*N*-dialkylanilines catalyzed by HPW in water




| Entry | Electrophile | Electron rich arene | Yield (%)[a] |
|---|---|---|---|
| 1 |  | 1 | 89 |
| 2 | | 2 | 93 |
| 3 | | 3 | N.R. |
| 4 |  | 1 | 90 |
| 5 | | 2 | 85 |
| 6 |  | 1 | 87 |
| 7 | | 2 | 85 |
| 8 |  | 1 | 92 |
| 9 |  | 1 | 83 |
| 10 | | 2 | 90 |
| 11 | | 1 | 92 |
| 12 |  | 2 | 95 |
| 13 |  | 1 | 85 |
| 14 | | 2 | 89 |
| 15 |  | 2 | 93 |
| 16 |  | 2 | 87 |
| 17 |  | 1 | 90 |
| 18 |  | 1 | N.R. |

[a] Reaction condition: *N*,*N*-dialkylaniline (2.2 mmol), nitroalkene (2 mmol), water (5 mL) and HPW (0.1 g, 0.035 mmol, 0.0175 mol%) at reflux temperature.

results are summarized in Table 1. Among the used catalysts, Only PTSA and $FeCl_3{\cdot}6H_2O$ gave 50% yields. Boric acid, $SnCl_2$, β-cyclodextrin, $ZrOCl_2{\cdot}8H_2O$ and CuCl gave low yield of product. With $CuCl_2$, $NiCl_2{\cdot}6H_2O$, Silica-sulfuric acid and DABCO trace amount of product was obtained. The results show the efficiency of HPW as catalyst in this reaction. With optimized conditions in hand, we then expanded our study to other electron-riched arenes and different nitroalkenes. As shown in Table 2, *N*,*N*-dimethylanilines and *N*,*N*-diethylaniline gave excellent yields. Also, nitroalkenes with electron-donating and electron-withdrawing groups on the phenyl ring gave excellent yields. Aliphatic nitroalkenes were also examined for this transformation without any result. Using 1,2-dimethoxy benzene as electron-riched arene did not afford any products and the starting material was recovered (Table 2, entry 3). Chalcones are not suitable electrophile in this reaction (Table 2, entry 18), which may be because of lower electrophilicity compare to nitroalkenes. Substitution was occurred only at the *para* position of the *N*,*N*-dialkylanilines and no *ortho* product was observed. Work-up was very simple; involving filtration of the solid products or decanting the water in most of the cases. Further purification was accomplished by using column chromatography if needed.

Theoretical calculations for determination of the optimized parameters (dipole moment, solvation energy, and partial charge on the *p*-position) of *N*,*N*-dimethylaniline and *N*,*N*-diethylaniline were performed with the HF/6-311G** basis set using Gaussian 03 software. As shown in Table 3, the dipole moment and the partial charge on the *p*-position of *N*,*N*-dialkylanilines in water are greater than in organic solvents, which may ascribe the higher

**Table 3**
Calculated parameters for *N*,*N*-dimethylaniline and *N*,*N*-diethylaniline in different solvents using the HF/6-311G** basis set.

| Solvent | N,N-dimethylaniline | | | N,N-diethylaniline | | |
|---|---|---|---|---|---|---|
| | $\mu$ (Debye)[a] | $\delta$[b] | $\Delta G^{\#}$[c] | $\mu$ (Debye)[a] | $\delta$[b] | $\Delta G^{\#}$[c,d] |
| Gas phase | 0.7362 | −0.4777 | – | 0.7109 | −0.5838 | – |
| Water | 1.1498 | −0.5629 | 4.03 | 1.2283 | −0.6424 | 5.91 |
| DMSO | 1.1033 | −0.5610 | 2.25 | 1.1845 | −0.6400 | 3.81 |
| THF | 1.0042 | −0.5438 | 2.64 | 1.0383 | −0.6281 | 4.10 |
| $CHCl_3$ | 0.9544 | −0.5344 | 2.05 | 0.9802 | −0.6223 | 3.27 |
| $CH_3CN$ | 1.1063 | −0.5601 | 4.35 | 1.1839 | −0.6395 | 6.24 |
| $CH_3NO_2$ | 1.1075 | −0.5603 | 2.12 | 1.1878 | −0.6396 | 3.60 |
| Toluene | 0.8543 | −0.5124 | 2.64 | 0.8532 | −0.6078 | 3.69 |
| Ethanol | 1.0900 | −0.5577 | −0.21 | 1.1662 | −0.6380 | 0.79 |
| Methanol | 1.1147 | −0.5595 | −0.3 | 1.1865 | −0.6401 | 0.70 |
| Acetone | 1.0795 | −0.5564 | 0.19 | 1.1536 | −0.6367 | 1.22 |

[a] Dipole moment for *N*,*N*-dialkylanilines in different solvents.
[b] Partial charge on C-4 of *N*,*N*-dialkylanilines.
[c] Solvation energy.
[d] PCM model was used to model solvation effect.

nucleophilic ability of the *p*-carbon toward nitroolefins. Also partial negative charge on the *p*-position in *N*,*N*-diethylaniline (−0.6424) is greater than in *N*,*N*-dimethylaniline (−0.5629), which confirm the higher electron donating ability of diethylamino group on phenyl ring related to dimethylamino group. In addition, the higher dipole moment of *N*,*N*-diethylaniline compare to *N*,*N*-dimethylaniline can be correlated to higher solvation energy which in gas phase the dipole moment is the reverse of this.

## 4. Conclusions

In conclusion, we have reported a mild, simple, and environmentally benign procedure for the Friedel–Crafts alkylation of *N*,*N*-dialkylanilines with nitroolefins in aqueous medium using heteropolyphosphotungstic acid as catalyst. This procedure offers several advantages including the use of green and low-loading catalyst, high to excellent yield, green solvent, cleaner reaction and simple experimental procedure, which make it a useful and attractive strategy in synthetic organic chemistry. In addition, water may play dual roles in this procedure as a solvent or as a co-catalyst. Water may accelerate the reaction *via* hydrogen bonding with nitroalkenes or increase the catalytic efficiency of heteropolyphosphotungstic acid by providing a homogenous medium with highly acidic strength. Theoretical studies also support our finding on the Friedel–Crafts alkylation on the *p*-position in phenyl ring and why the reaction is plausible in water compared to organic solvents.

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