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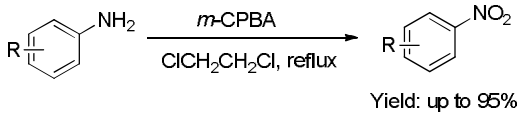

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Oxidation of Aromatic Amines into Nitroarenes with *m*-CPBA

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ABSTRACT

A versatile and highly efficient approach for the synthesis of nitroarenes from aromatic amine using *m*-CPBA has been developed. This oxidation reaction was operationally straightforward and proceeded to afford products in good isolated yields.

Nitro group has unique chemical properties such as being common explosophore used globally to make explosives and having strong electron withdraw effects applied in dyes, perfumes, pharmaceuticals and plastics.[1] Aromatic nitro compounds showed interesting applications as explosives and dyes as well as being the important starting material with broad applications such as the synthesis of indole[2] and indigo[3]. These aromatic nitro compounds were typically obtained from the electrophilic substitution reaction with the nitrating reagent such as a mixture of nitric acid and sulfuric acid.[4] Most of these classical methods were under harsh conditions as well as utilized hazardous reagents which could generate wastes to pose environmental problems.[5] Even though, many aromatic nitro compounds were difficult to obtain by the direct nitration of the aromatic ring or through nitration of anionic intermediates originating from alkyl halides, alkenes or ketones. Therefore, the oxidation of aromatic amines to corresponding nitroarenes should be an additional choice with the readily available oxidants. Several methods for the direct oxidation of aromatic amines into corresponding nitroarenes have been published already using pertrifluoroacetic acid[6a], dimethyldioxirane[6b], oxone®[6c], tetra-*n*-alkylammonium bromates[6d], and potassium iodide[6e] or $Rh_2(cap)_4$[6f] associate TBHP, etc..

Previously reported methodologies utilized *m*-chloroperbenzoic acid (*m*-CPBA) to oxidize the steroidal amines[7a], aliphatic amines[7c] and diamondoid amines[7e] into their corresponding nitro compounds[7]. However, the oxidation of aromatic amines was not conducted. In the present work, the oxidant *m*-CPBA was found to be also applicable for the preparation of nitroarenes. Herein, this report described an approach to various nitroarenes from aromatic amines with *m*-CPBA in 1,2-dichloroethane.

To explore the potential of this reaction, aniline **1a** was treated with *m*-CPBA under refluxing 1,2-dichloroethane. After several trials, using 4.0 equivalents of *m*-CPBA was found to be suitable. The effect of solvents was briefly investigated. The reaction in CH_3CN proceeded with lower yield (Table 1, entry 5) and the desired nitrobenzene **2a** could not be detected in THF (Table 1, entry 6). 1,2-dichloroethane was superior to other solvents (Table 1, entry 3).

To understand the substrate scope, a wide range of aromatic amines were tested under the optimized reaction condition (Table 2). Electron-donating or electron-withdrawing substituent produced good to excellent yields, indicating that the reaction was little sensitive to electronic effects. Interestingly, the synthesis of 4-nitroanisile **2b** could achieve at r.t. instead of refluxing (Table 2, entry 2). Under the present oxidation system, the steric effect of substrates was not significant. The transformations of substituted aromatic amines showed excellent tolerance of functional

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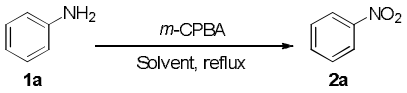
Table 1. Optimization of Reaction Conditions[a]



1a 2a

Entry	Solvent	*m*-CPBA(eq.)	Yields (%)[b]
1	$ClCH_2CH_2Cl$	3.3	Trace
2	$ClCH_2CH_2Cl$	3.8	72
3	$ClCH_2CH_2Cl$	4.0	81
4	$ClCH_2CH_2Cl$	4.5	77
5	CH_3CN	4.0	68
6	THF	4.0	ND[c]

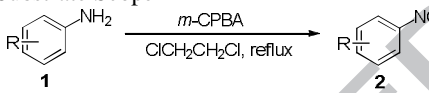
[a] Reaction conditions: aniline **1** (2.0 mmol), solvent (20.0 mL), N_2 atmosphere.

[b] Isolated yields.

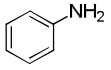
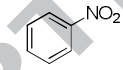
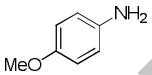
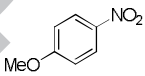
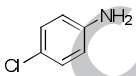
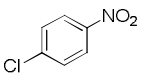
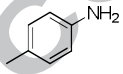
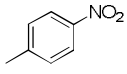
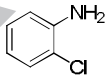
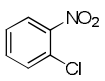
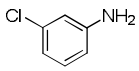
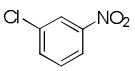
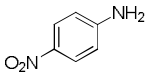
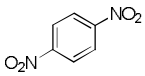
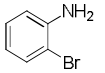
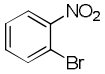
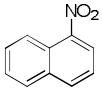
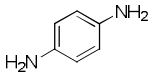
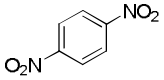
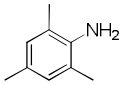
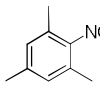
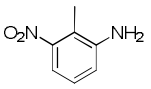
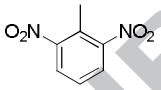
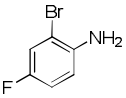
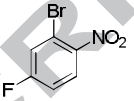
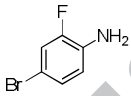
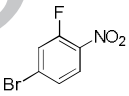
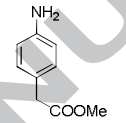
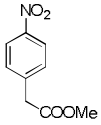
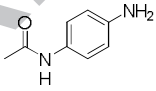
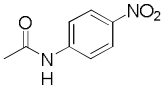
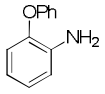
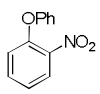
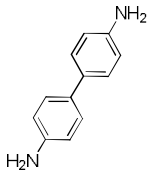
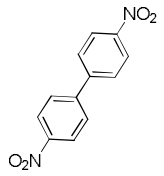
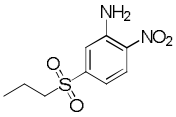
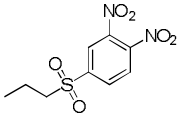
[c] ND: not determined.

groups including aromatic halides, ester (Table 2, entry 15), amide (Table 2, entry 16) and ethers (Table 2, entries 2 and 17). When strong electron-withdrawing groups such as sulfone or nitro group attached on the benzene ring alone, the reaction could still provide the target compounds with high yield (Table 2, entries 7, 12, and 21-22). Nevertheless, the reaction could not proceed at all with the substrates bearing nitro and sulfone group at the same time. (Table 2, entries 19-20). The oxidation of 1,4-benzendiamine **1j** could work by increasing the equivalents of *m*-CPBA to afford 1,4-dinitrobenzene **2g** (Table 2, entry10). However, benzidine **1r** could not produce nitro compounds even adjusting the reaction temperature and the amount of *m*-CPBA used (Table 2, entry 18).

Table 2. Substrate Scope[a]



1 2

Entry	Substrate		Product		Yield[b](%)
1		**1a**		**2a**	81
2[c]		**1b**		**2b**	95
3		**1c**		**2c**	85
4		**1d**		**2d**	80
5		**1e**		**2e**	78
6		**1f**		**2f**	81
7		**1g**		**2g**	80
8		**1h**		**2h**	74
9		**1i**		**2i**	58
10[d]		**1j**		**2g**	56
11		**1k**		**2k**	61
12		**1l**		**2l**	63
13		**1m**		**2m**	71
14		**1n**		**2n**	82
15		**1o**		**2o**	80
16		**1p**		**2p**	92
17		**1q**		**2q**	91
18[d]		**1r**		**2r**	ND[e]
19		**1s**		**2s**	NR[e]
20		**1t**		**2t**	NR[e]
21		**1u**		**2u**	78
22		**1v**		**2v**	87

[a] All reactions were performed under refluxing 1,2-dichloroethane with anilines (2.0 mmol) and *m*-CPBA (8.0 mmol) for 10 h, unless otherwise noticed.

[b] Isolated product.

[c] The reaction was carried out at r.t..

[d] The reaction was performed under refluxing 1,2-dichloroethane with diamines (2.0 mmol) and *m*-CPBA (16.0 mmol) for 10 h.
[e] ND: not determined, NR: no reaction.

In conclusion, an efficient and practical method for the synthesis of nitroarenes from aromatic amines using commercially available reagents *m*-CPBA was developed. The investigation of the profile of substrates was well demonstrated. The described chemistry expands the repertoire of reactions carried out by *m*-CPBA, a versatile oxidant with ever-increasing utility in chemical synthesis.

Acknowledgments

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9. *General procedure for the oxidation of aromatic amines with m-CPBA: m*-CPBA (1.7 g, 8.0 mmol, 85%) was dissolved in 1,2-dichloroethane (15.0 mL) in a three-neck flask equipped with a condenser and heated to reflux (at r.t. in case of **1b**). Then, the substrate aromatic amine (2.0 mmol) dissolved in 1,2-dichloroethane (5.0 mL) was added dropwise to the refluxing peracid solution. After 10 h, the mixture was cooled to r.t. and quenched with saturated aqueous $Na_2S_2O_3$. The solvent was removed under reduced pressure and the residue was treated with 10% NaOH solution followed by extraction with EtOAc. The combined extracts were washed with H_2O and brine, dried over anhydrous Na_2SO_4. Removal of the solvent under vacuum afforded the crude product, which was purified by column chromatography using hexane/ethyl acetate as eluant.

Nitrobenzene (2a)[8a]. Yellow oil, yield 81%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.3 Hz, 2H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.2, 134.6, 129.3, 123.5; GC-MS (*m/z*) $[M]^+$: 123 ($C_6H_5NO_2$, 123.03).

4-Nitroanisile (2b)[8b]. White solid, yield 95%; mp 50-51 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 9.0 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.6, 141.5, 125.9, 114.0, 55.9; GC-MS (*m/z*) $[M]^+$: 153 ($C_7H_7NO_3$, 153.04).

4-Nitrochlorobenzene (2c)[8b]. Yellow solid, yield 85%; mp 81-83 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21-8.17 (m, 2H), 7.54-7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.5, 141.4, 129.6, 124.9; MS (EI) *m/z*: 157 (100%), 159 (34%) $[M]^+$.

4-Nitrotoluene (2d)[8a]. Yellow solid, yield 85%; mp 52-53 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.2, 145.9, 129.8, 123.5, 21.6; MS (EI) *m/z*: 91 (100%), 137 (95%) $[M]^+$.

2-Nitrochlorobenzene (2e)[8c]. Yellow liquid, yield 78%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (dd, J_1 = 8.1 Hz, J_2 = 1.4 Hz, 1H), 7.57-7.52 (m, 2H), 7.44-7.42 (m, 1H); ^{3}C NMR (100 MHz, $CDCl_3$): δ = 148.1, 133.2, 131.9, 127.6, 127.0, 125.6; MS (EI) *m/z*: 111 (75%), 157 (100%), 159 (33%) $[M]^+$.

3-Nitrochlorobenzene (2f)[8a]. Light yellow solid, yield 81%; mp 45-46 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (t, *J* = 2.1 Hz, 1H), 8.14 (ddd, J_1 = 8.3 Hz, J_2 = 2.1 Hz, J_3 = 1.0 Hz, 1H), 7.69 (ddd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, J_3 = 1.0 Hz, 1H), 7.51 (t, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.8, 135.4, 134.7, 130.4, 123.9, 121.7; GC-MS (*m/z*) $[M]^+$: 157 ($C_6H_4ClNO_2$, 156.99).

1,4-Dinitrobenzene (2g). Yellow solid, yield 80%; mp 165-166 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.1, 124.9; MS (EI) *m/z*: 168 (100%) $[M]^+$.

1-Bromo-2-nitrobenzene (2h)[8c]. Yellow solid, yield 74%; mp 43-45 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86-7.83 (m, 1H), 7.76-7.74 (m, 1H), 7.49-7.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.9, 135.1, 133.2, 128.3, 125.6, 114.5; GC-MS (*m/z*) $[M]^+$: 201 ($C_7H_7NO_3$, 200.94); MS (EI) *m/z*: 155 (79%), 157 (79%), 201 (100%), 203 (100%) $[M]^+$.

1-Nitronaphthalene (2i). Yellow solid, yield 58%; mp 55-57 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (d, *J* = 8.7 Hz, 1H), 8.22 (dd, J_1 = 7.6 Hz, J_2 = 1.1 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.71 (ddd, J_1 = 8.6 Hz, J_2 = 7.0 Hz, J_3 = 1.3 Hz, 1H), 7.63-7.60 (m, 1H), 7.53 (dt, J_1 = 7.9 Hz, J_2 = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.6, 134.7, 134.4, 129.5, 128.6, 127.4, 125.1, 124.1, 124.0, 123.1; MS (EI) *m/z*: 127 (94%), 173 (100%) $[M]^+$.

1,3,5-Trimethyl-2-nitrobenzene (2k)[8d]. Pale yellow solid, yield 61%; mp 43-45 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.92 (s, 2H), 2.31 (s, 3H), 2.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.8, 140.3, 129.6, 129.4, 21.0, 17.5; MS (EI) *m/z*: 148 (100%), 165(62%) $[M]^+$.

2,6-Dinitrotoluene (2l). Pale yellow solid, yield 63%; mp 65-66 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.1 Hz, 2H), 7.53 (t, *J* = 8.1 Hz, 1H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.7, 127.5, 127.5, 127.3, 14.8; MS (EI) *m/z*: 165 (100%), 182 (3%) $[M]^+$.

2-Bromo-4-fluoro-1-nitrobenzene (2m)[8e]. Yellow solid, yield 71%; mp 42-43 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (dd, J_1 = 9.1 Hz, J_2 = 5.2 Hz, 1H), 7.49 (dd, J_1 = 7.8 Hz, J_2 = 2.7 Hz, 1H), 7.18 (ddd, J_1 = 9.1 Hz, J_2 = 7.2 Hz, J_3 = 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.7 (d, $^1J_{CF}$ = 260 Hz), 146.1, 127.9 (d, $^3J_{CF}$ = 10 Hz), 122.5 (d, $^2J_{CF}$ = 26 Hz), 116.4 (d, $^3J_{CF}$ = 11 Hz), 115.5 (d, $^2J_{CF}$ = 23 Hz); ^{19}F (376 MHz, $CDCl_3$): δ = -

102.9--103.0 (m, 1F); MS (EI) *m/z*: 189 (99%), 191 (100%), 219 (96%), 221 (97%) $[M]^+$.

4-Bromo-2-fluoro-1-nitrobenzene (2n)[8e]. Yellow solid, yield 82%; mp 86-88 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (t, *J* = 8.3 Hz, 1H), 7.52-7.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.4 (d, $^1J_{CF}$ = 270 Hz), 138.5, 129.4 (d, $^3J_{CF}$ = 9 Hz), 128.1 (d, $^3J_{CF}$ = 4 Hz), 127.2 (d, $^4J_{CF}$ = 3 Hz), 122.1 (d, $^2J_{CF}$ = 24 Hz); ^{19}F (376 MHz, $CDCl_3$): δ = -114.3--114.5 (m, 1F); HRMS (EI) *m/z* $[M]^+$ calculated for $C_6H_3BrFNO_2$: 220.9304, found: 220.9311.

Methyl nitrophenylacetate (2o)[8b]. Yellow solid, yield 80%; mp 53-54 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 3.75 (s, 2H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.6, 147.2, 141.3, 130.3, 123.7, 52.4, 40.7; MS (EI) *m/z*: 106 (100%), 195 (42%) $[M]^+$.

***N*-(4-Nitrophenyl)ethanamide (2p)[8f].** Pale yellow solid, yield 92%; mp 210-211 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.54 (s, 1H), 8.21 (d, *J* = 9.1 Hz, 2H), 7.82 (d, *J* = 9.2 Hz, 2H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 169.3, 145.4, 142.0, 124.9, 118.5, 24.2; HRMS (EI) *m/z* $[M]^+$ calculated for $C_8H_8N_2O_3$: 180.0535, found: 180.0536.

1-Nitro-2-phenoxybenzene (2q)[8g]. Light yellow liquid, yield 91%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (dd, J_1 = 8.2 Hz, J_2 = 1.6 Hz, 1H), 7.52-7.46 (m, 1H), 7.40-7.36 (m, 2H), 7.18 (ddd, J_1 = 7.4 Hz, J_2 = 3.3 Hz, J_3 = 1.4 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 7.01 (dd, J_1 = 8.4 Hz, J_2 = 0.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 149.7, 140.4, 133.1, 129.0, 124.7, 123.6, 122.1, 119.4, 118.2; HRMS (EI) *m/z* $[M]^+$ calculated for $C_{12}H_9NO_3$: 215.0582, found: 215.0582.

1-Methanesulfonyl-4-nitrobenzene (2u). Pale yellow solid, yield 78%; mp 133-134 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, *J* = 8.1 Hz, 2H), 8.17 (d, *J* = 8.2 Hz, 2H), 3.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.8, 145.9, 128.9, 124.6, 44.2; HRMS (EI) *m/z* $[M]^+$ calculated for $C_7H_8N_7O_4S$: 201.0096, found: 201.0097.

1-Methanesulfonyl-3-nitrobenzene (2v). Pale yellow solid, yield 87%; mp 137-138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (s, 1H), 8.54 (d, *J* = 8.1 Hz, 1H), 8.31 (d, *J* = 7.8 Hz, 1H), 7.85 (t, *J* = 8.0 Hz, 1H), 3.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.5, 142.6, 133.1, 131.0, 128.3, 123.0, 44.4; HRMS (EI) *m/z* $[M]^+$ calculated for $C_7H_8N_7O_4S$: 201.0096, found: 201.0098.