



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.

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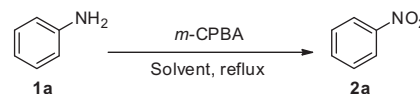
Nitro group has unique chemical properties such as being common explosive used globally to make explosives and having strong electron withdrawing effects applied in dyes, perfumes, pharmaceuticals, and plastics.¹ Aromatic nitro compounds showed interesting applications as explosives and dyes as well as being the important starting material with broad applications such as the synthesis of indole² 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 Rh₂(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 Letter 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.⁹ After several trials, using 4.0 equiv of *m*-CPBA was found to be suitable. The effect of solvents was briefly investigated. The reaction in CH₃CN 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).

Table 1
Optimization of reaction conditions^a



Entry	Solvent	<i>m</i> -CPBA (equiv)	Yields ^b (%)
1	ClCH ₂ CH ₂ Cl	3.3	Trace
2	ClCH ₂ CH ₂ Cl	3.8	72
3	ClCH ₂ CH ₂ Cl	4.0	81
4	ClCH ₂ CH ₂ Cl	4.5	77
5	CH ₃ CN	4.0	68
6	THF	4.0	ND ^c

^a Reaction conditions: aniline **1** (2.0 mmol), solvent (20.0 mL), N₂ atmosphere.

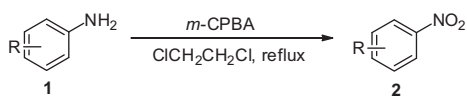
^b Isolated yields.

^c ND: not determined.

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Table 2
Substrate scope^a



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

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