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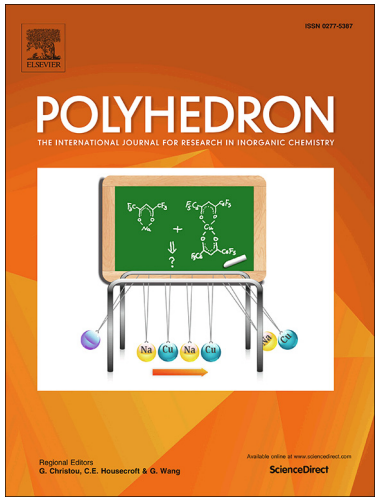

Bismuth Nitrate as a Source of Nitro Radical in *Ipso*-Nitration of Carboxylic Acids

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Bismuth Nitrate as a Source of Nitro Radical in *Ipso*-Nitration of Carboxylic Acids

Soumitra Agasti,[+] Siddhartha Maiti,[¶] Soham Maity,[+] M. Anniyappan,[§] M. B. Talawar,*[,§] and Debabrata Maiti[+,*]

[+]*Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai, 400076, India* ***Email: dmaiti@chem.iitb.ac.in***

[¶]*Department of Biosciences and Bioengineering, Indian Institute of Technology Bombay, Powai, Mumbai, 400076, India*

[§]*High Energy Materials Research Laboratory Pune (HEMRL), Ministry of Defense Research and Development Organisation, *Email: talawar.mb@hemrl.drdo.in*

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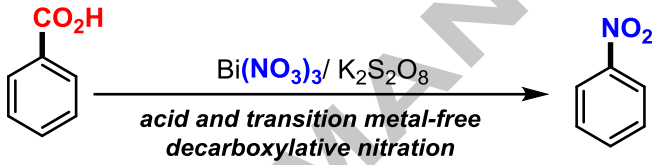


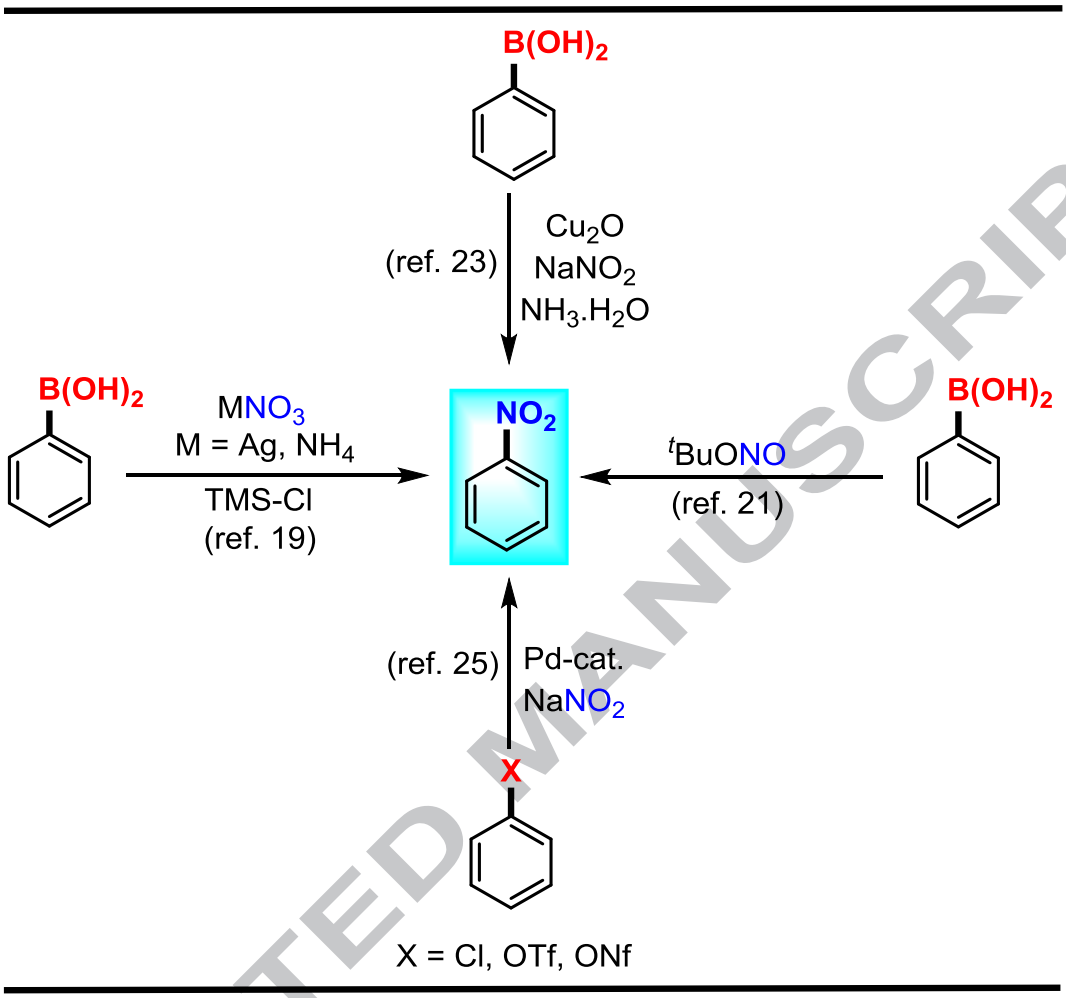
ABSTRACT

Aromatic nitro compounds are extensively used in synthetic chemistry. We disclose a new approach to obtain nitroarenes regioselectively starting from carboxylic acids under acid-free reaction conditions.

INTRODUCTION

Nitroarenes are extensively used in synthetic chemistry for the preparation of pharmaceuticals,[1] explosives,[2] dyes,[3] materials[4] etc.[5] Consequently, selective incorporation of nitro group onto an arene has drawn significant attention in recent years.[6-11] Conventional synthesis of nitroarenes primarily relied upon mixed acid reagents (HNO_3/H_2SO_4) for decades and was restricted by harsh condition, limited functional group tolerance, poor substrate scope and formation of undesired mixture of regioisomers or oxidized by-products.[6]

Scheme 1.Previous Approaches of *ipso*-Nitration

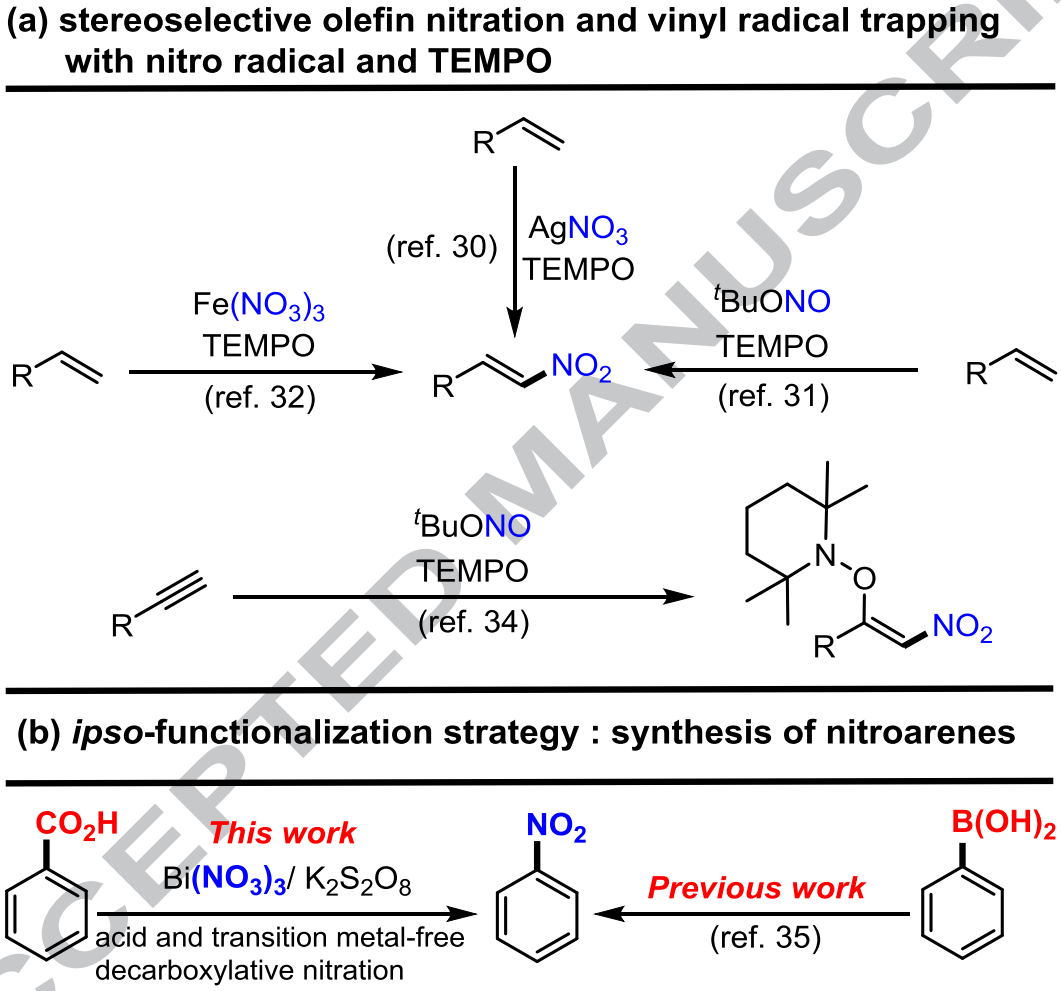


An alternative approach made use of *ipso*-functionalization strategy to circumvent these problems,[12] wherein nitro group was introduced in a regioselective manner under user-friendly conditions.[13] Arylboronic acids were selected as a fitting candidate for this purpose due to its successful application in a number of C–C and C–X bond formations and cross coupling reactions.[14-18]

Nitrodeboronation pathway dominated the regioselective synthesis of aromatic nitro compounds (Scheme 1).[19-24] On the other hand, starting from aryl chlorides, triflates and nonaflates, Pd-catalyzed nitration reactions expanded the scope of nitroarene synthesis (Scheme 1).[25-27] Recently,

chelation assisted *ortho* C–H functionalization has also been employed to introduce nitro group in a regioselective manner.[28, 29]

Scheme 2. Our Previous Work on Unsaturated Systems and *ipso*-Functionalization Strategy with Nitro Radical

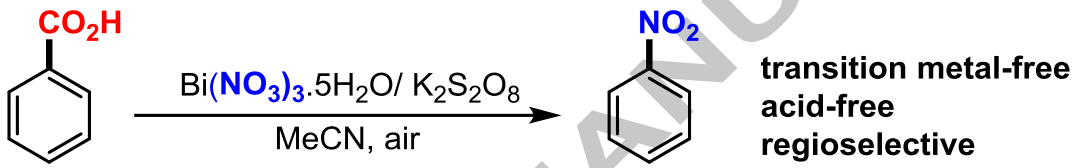


We have previously reported a number of efficient nitration reactions through radical pathway (Scheme 2).[30-34] During the course of our study, we noticed that bismuth nitrate can be utilized as a source of nitro radical with inorganic oxidant $K_2S_2O_8$.[35-37] In this context, a decarboxylative nitration,[38-40] if developed would be highly interesting since carboxylic acids are widely

available.[41, 42] Furthermore, carboxylic acids can be prepared easily and handled without much care.[43-52]

Notably, transition metal catalyzed radical protodecarboxylations are well known and intermediacy of an aryl radical has been suggested.[53-57] Intrigued by the prospect of trapping this aryl radical intermediate with an *in-situ* generated nitro radical, we set out to explore an *ipso*-nitration starting from arylcarboxylic acids (Scheme 3).

Scheme 3.*ipso*-Nitration of Carboxylic Acids

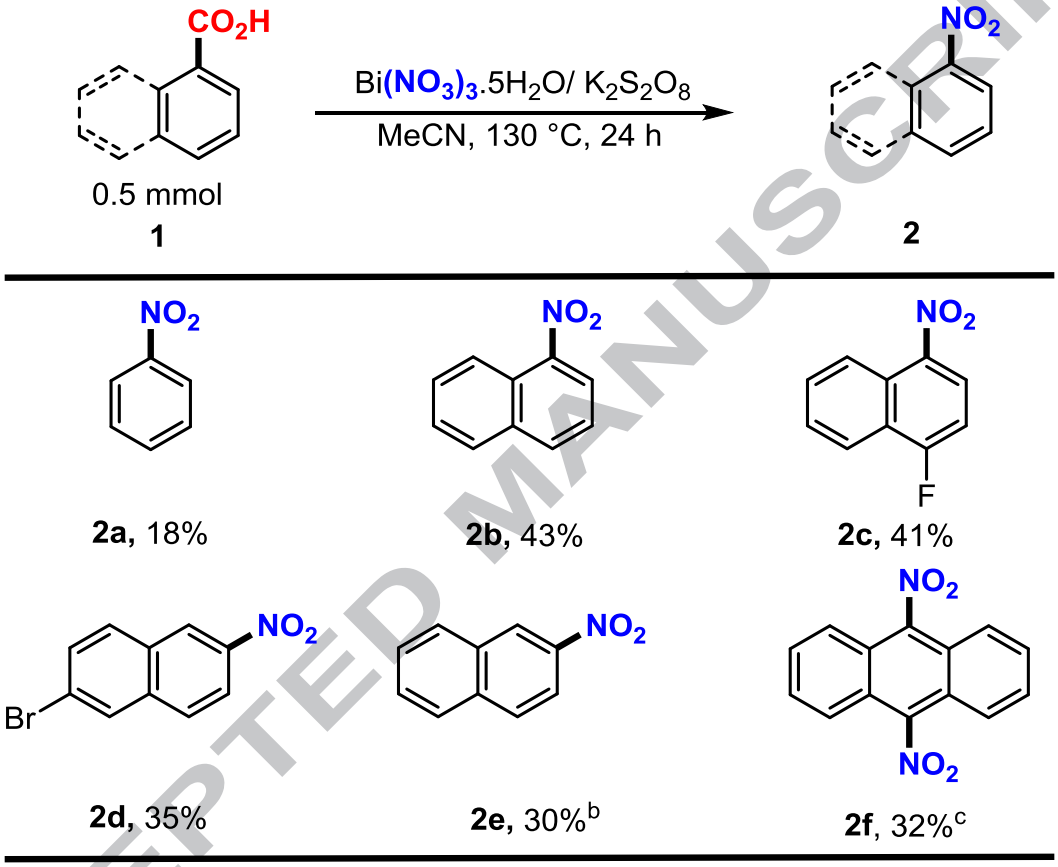


RESULTS AND DISCUSSION

Preliminary investigations in different solvents indicated that nitroarenes indeed could be generated though the initial yield was only 5%. Different nitrate/nitrite salts such as $Fe(NO_3)_3.9H_2O$, $Pb(NO_3)_3$, $AgNO_2$ etc. were investigated as potential nitrating agents but only trace amount of nitroarenes was detected. Interestingly, use of catalytic Ag-salts as an additive had no effect on the reaction outcome. It was rather surprising in view of its unique ability to trigger decarboxylation at an elevated temperature.[53-55, 58, 59] Use of different bases also did not alter the outcome to a significant extent.[60] After extensive optimization with several reaction parameters, we found that 2 equiv. of $Bi(NO_3)_3$ and 3.5 equiv. of $K_2S_2O_8$ could generate nitrobenzene in 18% isolated yield in acetonitrile (MeCN) at 130 °C. Such an elevated reaction temperature was accounted for the high activation energy of the decarboxylation step. After

thorough optimization study we could not find a better solvent than acetonitrile to reduce the excess pressure in the reaction setup. Note that 70% of unreacted benzoic acid (starting material) was isolated from this reaction.

Scheme 4. Nitration of Aromatic Carboxylic Acids[a]



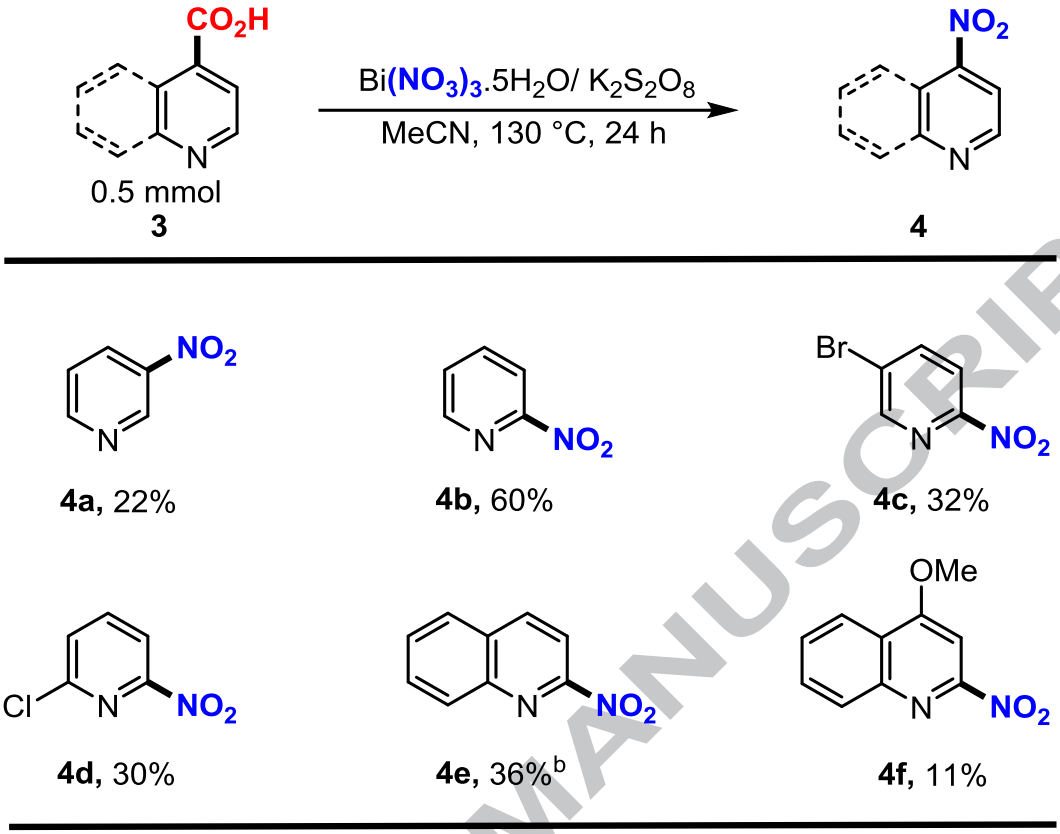
[a]Reaction conditions: ArCOOH (0.5 mmol), $Bi(NO_3)_3.5H_2O$ (2 equiv.), $K_2S_2O_8$ (3.5 equiv.), MeCN (3 mL), 130 °C, 24 h, air. Note that unreacted ArCOOH was isolated from each of these reaction.[60] [b]Trace amount of α-isomer was formed. [c]Starting from anthracene-9-carboxylic acid.

Next, we decided to investigate the scope of the reaction with other aromatic carboxylic acids (Scheme 4). 1-Naphthoic acid exhibited increased formation of nitro product up to 43% isolated

yield under the standard condition (**2b**). The 4-fluoronaphthoic acid gave desired product in 41% yield (**2c**). Similarly, 2-napthoic acid and its bromo derivative underwent decarboxylative nitration under the present reaction conditions (**2d** and **2e**). However, anthracene-9-carboxylic acid gave dinitro product in 32% isolated yield (**2f**).

Encouraged by these results we applied the standard condition on heteroaromatic carboxylic acids based on pyridines and quinolines (Scheme 5). Notably, incorporation of electrophilic nitro group on electron deficient heteroarenes remained an unsolved problem so far. Nicotinic acid indicated that nitration could be performed on such moiety (**4a**, 22%). 2-Picolinic acid gave the desired product in an improved 60% isolated yield. However, presence of bromo and chloro group at different positions substantially decreased the yield (**4c** and **4d**). Quinoline-2-carboxylic acid also underwent successful nitration. Reaction with related 4-methoxy-quinoline-2-carboxylic was sluggish and nitroarene product was obtained in 11% yield.

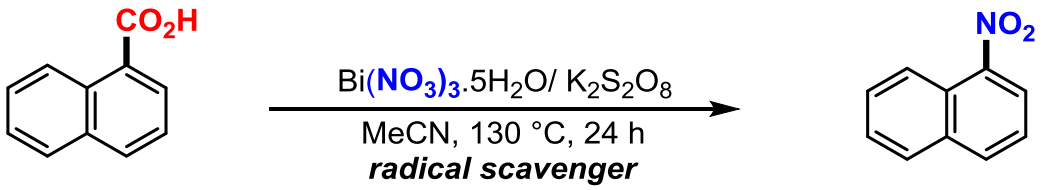
Scheme 5. Nitration of Heteroaromatic Carboxylic Acids[a]



[a]Reaction conditions: ArCOOH (0.5 mmol), $Bi(NO_3)_3.5H_2O$ (2 equiv.), $K_2S_2O_8$ (3.5 equiv.), MeCN (3 mL), 130 °C, 24 h, air. Note that unreacted arylcarboxylic acid was isolated from each of these reaction.[60] [b]Mixture of 2-nitroquinoline and 3-nitroquinoline (yield determined by GC).

We hypothesized that the reaction proceeded through a mechanism involving radical intermediates. To verify our hypothesis, a series of experiments with radical scavengers were performed. Radical quenchers like TEMPO, HOBT and 2, 4, 6-tri *tert*-butylphenol was added in the reaction mixture under standard reaction conditions.

Table 1. Reaction with Radical Scavengers



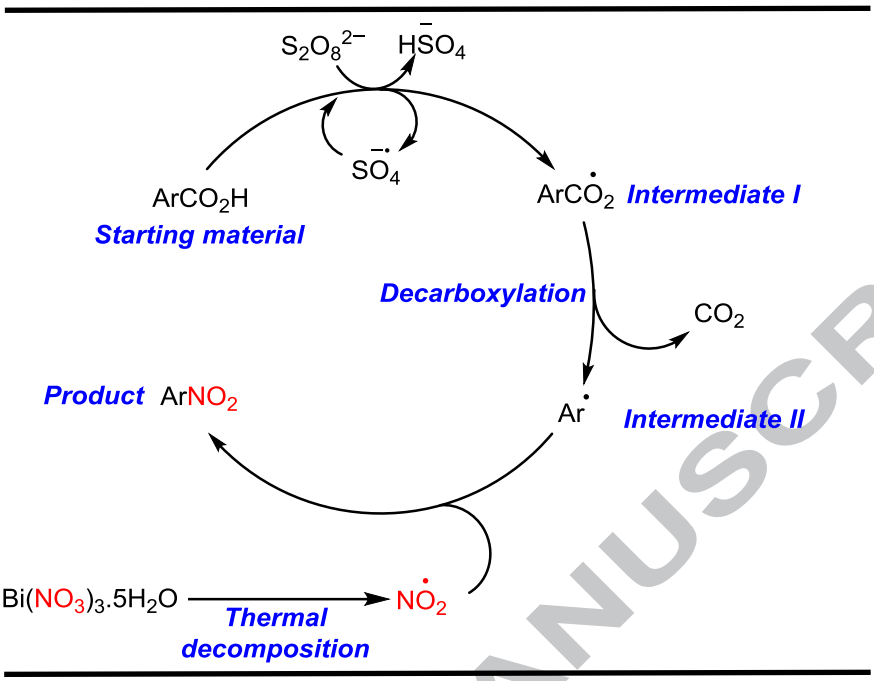
Entry	radical scavenger	yield (%)[b]
1	-	45
2	TEMPO	18
3	HOBT	5
4	2, 4, 6-tri *tert*-butylphenol	18

[a]Reaction conditions: ArCOOH (0.25 mmol), $Bi(NO_3)_3.5H_2O$ (2 equiv.), $K_2S_2O_8$ (3.5 equiv.), MeCN (2 mL), 130 °C, 24 h, air, 0.5 mmol scavenger. [b]Yields determined by GC.

In presence of TEMPO, desired 1-nitronaphthalene was formed only in 18% yield (Table 1). HOBT and 2, 4, 6-tri *tert*-butylphenol also quenched the reaction significantly and gave 5% and 8% yields, respectively. However, 45% yield of 1-nitronaphthalene has been detected without any scavenger. Significant decrease of product formation in presence of radical scavenger indicates in favor of aryl radical formation, which was quenched in the reaction medium.

Based on these experimental observations, a radical based pathway is described in Scheme 6. Under heating condition, homolytic cleavage of perdisulfate anion will produce sulphate radical anion.[7] This sulphate radical anion will capture hydrogen radical from starting material and as a result **intermediate I** will form along with hydrogen sulphate.[16, 61] In situ removal of CO_2 from **intermediate I** will generate aryl radical species.[15, 62] Under elevated temperature, bismuth nitrate will produce nitro radical and this nitro radical will be intercepted by aryl radical species to give desired nitro arene.[35]

Scheme 6. An Outline of the Possible Mechanistic Pathway



CONCLUSION

In conclusion, we have discovered that carboxylic acids can be converted to nitroarenes by an *ipso*-nitration reaction with $Bi(NO_3)_3/K_2S_2O_8$. Both aromatic and hetero aromatic carboxylic acids were converted to the nitroarenes under an acid-free condition. Although low to moderate yields are obtained at present, such a cost-effective method is expected to trigger systematic development of decarboxylative nitration reactions. From initial understanding, a radical pathway seemed to be operative. Further improvement of the decarboxylative nitration methodology, synthetic application and mechanistic details are the subject of our present research.

EXPERIMENTAL SECTION

General Procedure A for Decarboxylative Nitration of Aryl Carboxylic acid:

An oven dried resealable screw cap standard reaction tube containing a magnetic stir bar was charged with potassium persulfate (1.75 mmol, 472.5 mg), bismuth nitrate (1.0 mmol, 486mg). Then aryl carboxylic (0.5 mmol) was introduced in this mixture followed by acetonitrile (3 mL) was added in it. The tube was placed in a preheated oil bath at 130 °C and the reaction mixture was stirred vigorously for 24 h in air atmosphere. The reaction mixture was cooled to room temperature, diluted with 2 mL ethyl acetate and filtered through celite, eluting with additional 10 mL of ethyl acetate. The filtrate was concentrated and the resulting residue was purified by column chromatography.

Nitrobenzene: (Scheme 4, entry 2a) (liquid) Isolated yield=18%. Recovered Starting Material (R.S.M) 68%: 1H NMR (400 MHz, Chloroform-d) δ: 7.52 (tt, *J* = 7.7, 7.7, 1.4, 1.4 Hz, 2H), 7.68 (td, *J* = 7.5, 7.4, 1.2 Hz, 1H), 8.16 – 8.21 (m, 2H). **13C NMR** (101 MHz, CDCl3) δ: 123.49, 129.39, 134.72, 148.18. **GCMS (m/z):** 123.0[M]+

1-nitronaphthalene :(Scheme 4, entry 2b) (solid) Isolated yield=43% (R.S.M-39%): 1H NMR (400 MHz, Chloroform-d) δ: 7.53 (t, *J* = 8.0, 8.0 Hz, 1H), 7.61 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.71 (ddd, *J* = 8.6, 6.9, 1.4 Hz, 1H), 7.95 (ddt, *J* = 8.2, 1.3, 0.6, 0.6 Hz, 1H), 8.11 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.22 (dd, *J* = 7.6, 1.2 Hz, 1H), 8.56 (dq, *J* = 8.8, 0.9, 0.9, 0.9 Hz, 1H). **13C NMR** (101 MHz, CDCl3) δ: 123.26, 124.19, 124.30, 125.27, 127.52, 128.78, 129.62, 134.49, 134.85, 146.72. **GCMS (m/z):** 173.1[M]+

1-fluoro-4-nitronaphthalene: (Scheme 4, entry 2c) (solid) Isolated yield=41% (R.S.M-36%): 1H NMR (400 MHz, Chloroform-d) δ: 7.22 (td, *J* = 8.9, 8.9, 2.6 Hz, 1H), 7.71 (dddd, *J* = 8.2, 6.9, 2.7, 1.1 Hz, 1H), 7.81 (dddd, *J* = 8.6, 6.9, 2.7, 1.4 Hz, 1H), 8.23 (dt, *J* = 8.4, 1.6, 1.6 Hz, 1H), 8.31

– 8.35 (m, 1H), 8.70 (ddt, *J* = 9.0, 2.1, 1.0, 1.0 Hz, 1H). **13C NMR** (101 MHz, CDCl3) δ: 108.39, 108.62, 121.48, 123.80, 125.81, 125.92, 127.96, 130.79, 160.86, 163.48. **GCMS (m/z):** 191.1[M]+

2-bromo-6-nitronaphthalene: (Scheme 4, entry 2d) (solid) Isolated yield=35% (R.S.M-37%): 1H NMR (400 MHz, Chloroform-d) δ: 7.72 – 7.76 (m, 1H), 7.90 (t, *J* = 9.6, 9.6 Hz, 2H), 8.10 – 8.16 (m, 1H), 8.28 (dd, *J* = 9.0, 2.3 Hz, 1H), 8.77 – 8.80 (m, 1H). **13C NMR** (101 MHz, CDCl3) δ: 120.71, 124.65, 124.82, 128.85, 130.44, 130.62, 131.60, 131.79, 136.87, 145.86. **GCMS (m/z):** 252.0[M]+

2-nitronaphthalene: (Scheme 4, entry 2e) (solid) Isolated yield=30% (R.S.M-33%):1H NMR (400 MHz, Chloroform-d) δ: 7.67 (dddd, *J* = 21.7, 8.2, 6.9, 1.3 Hz, 2H), 7.92 – 7.99 (m, 2H), 8.03 (ddt, *J* = 8.0, 1.3, 0.7, 0.7 Hz, 1H), 8.24 (dd, *J* = 9.0, 2.3 Hz, 1H), 8.80 (dd, *J* = 2.3, 0.7 Hz, 1H). **13C NMR** (101 MHz, CDCl3) δ: 119.46, 124.84, 128.11, 128.19, 129.74, 129.93, 130.19, 132.13, 136.02, 145.68. **GCMS (m/z):** 173.0[M]+

9,10-dinitroanthracene : (Scheme 4, entry 2f) (solid) Isolated yield=32% (R.S.M-35%): 1H NMR (400 MHz, Chloroform-d) δ: 7.81 (dd, *J* = 5.8, 3.3 Hz, 4H), 8.29 – 8.36 (m, 4H). **13C NMR** (101 MHz, CDCl3) δ: 127.44, 133.73, 134.33, 183.36. **GCMS (m/z):** 268.2[M]+

3-nitropyridine : (Schem 5, entry 4a) Isolated yield=22% (R.S.M-56%):1H NMR (400 MHz, Chloroform-d) δ: 7.55 (ddd, *J* = 8.4, 4.8, 0.8 Hz, 1H), 8.51 (ddd, *J* = 8.4, 2.7, 1.5 Hz, 1H), 8.93 (dd, *J* = 4.8, 1.5 Hz, 1H), 9.47 (d, *J* = 2.8 Hz, 1H). **13C NMR** (101 MHz, CDCl3) δ: 124.03, 131.27, 145.38, 146.26, 155.08. **GCMS (m/z):** 124.0[M]+

2-nitropyridine :(Scheme 5, entry 4b) Isolated yield=60% (R.S.M-23%): 1H NMR (400 MHz, Chloroform-d) δ: 7.70 (ddd, *J* = 7.5, 4.7, 1.0 Hz, 1H), 8.07 (ddd, *J* = 8.1, 7.5, 1.8 Hz, 1H), 8.28 (dt, *J* = 8.2, 0.9, 0.9 Hz, 1H), 8.68 (ddd, *J* = 4.6, 1.9, 0.8 Hz, 1H). **13C NMR** (101 MHz, CDCl3) δ: 118.22, 129.36, 140.12, 149.22. **GCMS (m/z):** 124.1[M]+

5-bromo-2-nitropyridine :(Scheme 5, entry 4c) Isolated yield=32% (R.S.M-39%): 1H NMR (400 MHz, Chloroform-d) δ: 8.18 (t, *J* = 1.3, 1.3 Hz, 2H), 8.71 (q, *J* = 1.4, 1.4, 1.4 Hz, 1H). **13C NMR** (101 MHz, CDCl3) δ: 119.56, 127.27, 142.60, 150.36. **GCMS (m/z):** 202.9[M]+

2-chloro-6-nitropyridine :(Scheme 5, entry 4d) Isolated yield=30% (R.S.M-44%): 1H NMR (400 MHz, Chloroform-d) δ: 7.48 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.83 (t, *J* = 7.8, 7.8 Hz, 1H), 8.12 (dd, *J* = 7.6, 0.9 Hz, 1H). **13C NMR** (101 MHz, CDCl3) δ: 121.37, 127.60, 140.19, 150.04, 150.39. **GCMS (m/z):** 158.5[M]+

4-methoxy-2-nitroquinoline :(Scheme 5, entry 4f) Isolated yield=11% (R.S.M-63%): 1H NMR (400 MHz, Chloroform-d) δ: 4.15 (s, 3H), 7.63 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 1H), 7.68 (s, 1H), 7.79 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 8.07 (dt, *J* = 8.5, 0.9, 0.9 Hz, 1H), 8.23 – 8.27 (m, 1H). **13C NMR** (101 MHz, CDCl3) δ: 56.50, 97.85, 122.27, 122.79, 128.11, 129.68, 131.07, 147.50, 164.31, 172.30. **GCMS (m/z):** 204.1[M]+

ASSOCIATED CONTENTS

Keywords

Nitration; nitro radical; decarboxylation

Notes

The authors declare no competing financial interest.

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Supporting Information

Figures giving ^{1}H and ^{13}C NMR of all the compounds and details of the optimization study is available in the supporting information. Supplementary data to this article can be found online at https://doi.org/10.xxxx/j.poly.2019.xxx

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