

PEROXY COMPOUNDS AS ECO-FRIENDLY CATALYSTS FOR NITRATION OF AROMATIC COMPOUNDS USING SODIUM NITRITE IN AQUEOUS BISULFATE MEDIUM

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ABSTRACT

Peroxy compounds such as H₂O₂, peroxydisulfate (PDS), peroxymonosulfate (PMS), sodium perborate (SPB), and *tert*-butyl hydroperoxide (TBHP) have been used as efficient catalysts for nitration of aromatic and heteroaromatic compounds in presence of NaNO₂/KHSO₄ under mineral acid-free conditions. The reactions afforded very good yields of under different conditions. Depending on the nature of peroxide and substrate, reaction times recorded under conventional conditions reduced from (2 to 7hrs) hours to (25 to 60) minutes with grindstone technique, which in turn reduced to (25 to 120) seconds in microwave assisted reactions. Product yields are also increased from 6 to 10% under microwave irradiation as compared to conventional procedures. All synthesized compounds were characterized by ¹H NMR and mass spectral studies.

Keywords: H₂O₂, peroxydisulfate, peroxymonosulfate, sodium perborate, *tert*-butyl hydroperoxide; nitration; Grindstone technique; microwave irradiation; rate accelerations.

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INTRODUCTION

Nitration of aromatic and heteroaromatic compounds occupies one of the most important and forefront positions in the fields of electrophilic aromatic substitution reactions. Large numbers of nitroarenes are widely used as important intermediates and precursors during the synthesis of organic and organometallic compounds, pharmaceuticals, explosives, dyes, polymers, pesticides, plastics, drugs, and medicines, which make nitration of aromatic compounds as an area of evergreen interest to synthetic chemists.¹⁻³ The most popular and oldest classical method of nitration is the mixed acid or an acid mixture method (mixture of two strong acids, sulfuric and nitric acid) which is still popular and in use.¹ However, few nitration protocols also involved the use of nitric acid diluted in water or acetic acid. But the classical method of nitration is a notoriously polluting process because it generates large quantities of hazardous waste acid streams. These outlets are root causes of the environmental pollution. Besides, this separation of the nitro products from the acid is often a difficult and energy consuming process that implies a basic aqueous work-up. To overcome these issues, several modified protocols have been developed over the years.³⁻²⁰ One of the forefront reagents developed in direction is nitronium tetrafluoroborate, [(NO₂)⁺(BF₄)⁻], which has several advantages over nitric acid, apart from supplementing isolated the active nitronium ion ingredient.³ There are several other protocols that avoided the use of sulfuric acid completely, but used small amounts of HNO₃ along with other co-catalysts to accomplish nitration.⁴⁻¹⁴ Micelle-forming surfactants,¹⁵⁻¹⁷ supported catalysts such as P₂O₅ immobilized on silica gel,¹⁸ metal-modified montmorillonite,¹⁹ Al(H₂PO₄)₃ (ref.20), and V(V) heteropolyacids²¹ have also been used as efficient catalysts to synthesize nitroaromatic compounds in the presence of dilute HNO₃. Literature reports also revealed the use of an array of metal nitrates²²⁻³¹ and melamine nitrate³² were also used as effective nitrating agents for the synthesis of nitro-organic compounds. Ipso nitration of aryl boronic acids was reported³³ in aqueous media using NaNO₂/Cu₂O/aqNH₃. Few acid-free nitration protocols³⁴⁻⁴² were also developed using NH₄NO₃/KHSO₄, N₂O₅ and ClNO₂, TBAD and TBAC with NaNO₂, quaternary ammonium nitrate, N₂O₅/SO₂, tertiary butyl nitrite, MeNO₂ with K₂CO₃/Al₂O₃. The efforts of

Paul Anastas and Warner⁴³⁻⁴⁵ to overcome several environmental and cost-provoking issues lead to the development of twelve points of green chemistry, which served as twelve commandments for the chemists and biochemists to design and propagate several environmentally safe and economically viable synthetic protocols. The use of solvent-free methods such as mortar-pestle⁴⁶⁻⁴⁹, and microwave irradiation⁵⁰⁻⁵³ techniques made a landmark in organic synthesis because these methods are not only solvent-free but also operationally simple and satisfy both economic and environmental demands by replacing the toxic solvents. These methods are also associated with ease of manipulation and in several cases enhanced selectivity. On the other hand, in the recent past, potassium bisulfate (KHSO₄) is explored as an eco-friendly, inexpensive, non-toxic, and easy available efficient green catalyst for various organic transformations under homogeneous and heterogeneous conditions.^{38,39} A review article published by Baghernejad³⁹ provides an excellent bibliography depicting an array of synthetic strategies in which KHSO₄ is used as a catalyst. In many cases, the catalyst was recovered, activated and reused for three to four consecutive times with only slight variation in the yields of the products. Encouraged by the striking catalytic applications of KHSO₄, we have developed certain nitration protocols using NaNO₂/ peroxo compounds for the synthesis of nitroarenes using small (millimolar) amounts of KHSO₄. The peroxo compounds such as H₂O₂, *tert*butyl hydroperoxide (TBHP), Potassium peroxydisulfate (K₂S₂O₈ or PDS), peroxy monosulfate (oxone or PMS), and sodium perborate (SPB) are used as catalysts in this study are laboratory benchtop chemicals and are environmentally safe and economically viable.

EXPERIMENTAL

The chemicals used in this study were procured from Avra, Aldrich, Arcos Organics or SD -fine chemicals. BUCHI B-545 capillary melting point apparatus was used to determine the melting points of the compounds. Bench mate model microwave oven (CEM-908010, 300W) was used to perform microwave assisted experiments in this study. Thin layer chromatography (TLC) experiments were carried out using Merck aluminum-backed 0.2 mm silica gel 60 F-254 plates. Merck silica gel 60 (230-400mesh) samples were used in column chromatography experiments. Varian VNMRS-400 MHz and Perkin Elmer FT-IR spectrometers were employed to record infrared (IR) and ¹H NMR spectra of the products obtained in this study. Chemical shifts are reported as values in ppm relative to CHCl₃ (7.26), and TMS was used as internal standard.

General procedure for synthesis of nitroarenes

Ten (10) mmol of the substrate (aromatic compounds), one (1.0) mmol of KHSO₄, one (1.0) mmol of Peroxide in an acetonitrile solvent and 2.0 mmol NaNO₂ were taken in a round bottom flask and the mixture was stirred under reflux conditions. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was treated with a NaHCO₃ solution. The organic layer was separated, dried over Na₂SO₄, and evaporated under vacuum. The crude product was purified by column chromatography using ethyl acetate –hexane as eluant to get pure product. Products thus obtained are characterized as nitro derivatives by spectroscopic methods.

Microwave assisted synthesis of nitroarenes

The constituents of the reaction such as 10 mmol of the substrate, 1 mmol of KHSO₄, 1 mmol of peroxide in acetonitrile solvent and 2.0 mmol NaNO₂ were taken in a clean conical flask at room temperature and placed in a microwave oven. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was further processed for the isolation of product as detailed previously.

Grindstone synthesis of nitroarenes

The constituents of the reaction such as 10 mmol of the substrate, 1.0 mmol of KHSO₄, 2.0 mmol of NaNO₂, and a catalytic amount (1 mmol) of peroxide are taken in a mortar and ground with a pestle under solvent free conditions. The progress of the reaction was monitored by TLC. After completion, the workup procedure to obtain the products is largely similar to the one discussed in the earlier section. Obtained results from all the methods are presented Tables-2 to 4.

Table-1: List of aromatic compounds and nitroarenes

Substrate	Product	Substrate	Product
(1a)Phenol	(2a) 2-NO ₂ Phenol	(1k) <i>p</i> -OH Phenol	(2k) 2- NO ₂ Benzene-1,4-diol
(1b) <i>o</i> -Cresol	(2b) 2-Me- 4-NO ₂ Phenol	(1l) <i>p</i> -Nitro Phenol	(2l) 2,4- <i>di</i> Nitro Phenol
(1c) <i>p</i> -Cresol	(2c) 2-NO ₂ 4-Me Phenol	(1m) <i>p</i> -Amino Phenol	(2m) 2-Nitro4-Amino Phenol
(1d) <i>m</i> -Cresol	(2d) 3-Me- 4-NO ₂ Phenol	(1n) α -Naphthol	(2n) 2- NO ₂ -1-Naphthol
(1e) <i>o</i> - Cl Phenol	(2e) 4-NO ₂ 2-Cl Phenol	(1o) β -Naphthol	(2o) 1-NO ₂ -2-Naphthol
(1f) <i>m</i> - Cl Phenol	(2f) 4-NO ₂ 3-Cl Phenol	(1p)Aniline	(2p) 4-Nitro Aniline
(1g) <i>p</i> -Cl Phenol	(2g) 2-NO ₂ 4-Cl Phenol	(1q)Salicylic acid	(2q) 2-OH 4-NO ₂ Benzoic acid
(1h) <i>p</i> -Br Phenol	(2h) 2-NO ₂ 4-Br Phenol	(1r)Furan	(2r) 2-NO ₂ furan
(1i) <i>O</i> -OH Phenol	(2i) 4- NO ₂ Benzene-1,2-diol	(1s)Thiophene	(2s) 2-NO ₂ thiophene
(1j) <i>m</i> -OH Phenol	(2j) 4- NO ₂ Benzene-1,3-diol	(1t)Pyrrole	(2t) 2-NO ₂ Pyrrole

Table-2: Peroxy compound/NaNO₂ driven Nitration of Aromatic compounds in aq. KHSO₄ medium

Entry codes		PDS		PMS		H ₂ O ₂		TBHP		SPB	
Substrate	Product	RT (hr)	% Yield	RT (hr)	% Yield	RT (hr)	% Yield	RT (hr)	% Yield	RT (hr)	% Yield
(1a)	(2a)	2	70	4	70	5	70	5	68	7	68
(1b)	(2)	2	70	4	68	5	70	5	70	7	70
(1c)	(2c)	2	75	4	74	5	75	5	75	7	75
(1d)	(2d)	2	70	4	68	5	65	5	65	7	65
(1e)	(2e)	4	80	6	80	6	75	6	75	8	75
(1f)	(2f)	4	78	6	78	6	75	6	75	8	75
(1g)	(2g)	4	80	6	80	6	75	6	75	8	70
(1h)	(2h)	4	75	6	77	6	75	6	75	8	74
(1i)	(2i)	3	85	4	80	5	80	5	78	7	75
(1j)	(2j)	3	80	4	77	5	80	5	80	7	75
(1k)	(2k)	3	80	4	80	5	78	5	78	7	75
(1l)	(2l)	4	75	6	75	7	75	8	70	10	70
(1m)	(2m)	3	80	6	80	7	78	7	75	9	75
(1n)	(2n)	2	85	4	80	4	80	4	80	5	80
(1o)	(2o)	3	85	5	80	5	80	5	75	6	75
(1p)	(2p)	2	75	4	75	5	75	5	70	5	70
(1q)	(2q)	3	75	5	75	6	75	7	75	7	75
(1r)	(2r)	2	70	4	70	5	70	5	68	6	65
(1s)	(2s)	2	75	4	75	5	73	5	70	6	70
(1t)	(2t)	1	80	3	80	4	75	4	70	4	70

Table-3: Grindstone protocol for Peroxy compound/NaNO₂/KHSO₄ driven Nitration of Aromatic compounds under solvent-free conditions

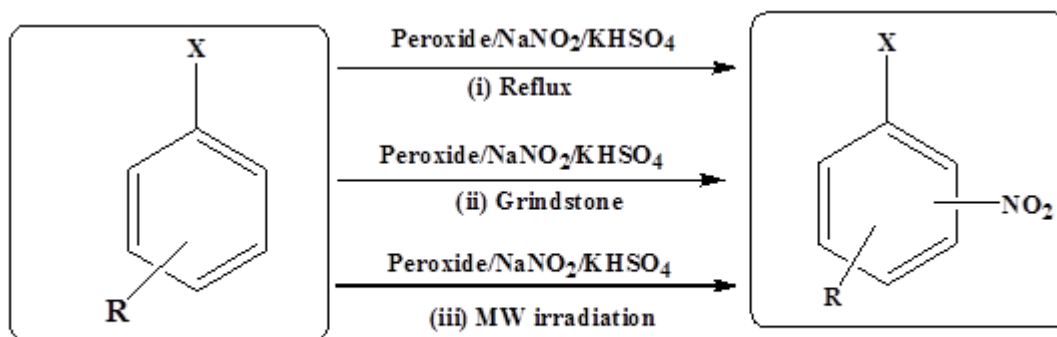
Entry codes		PDS		PMS		H ₂ O ₂		TBHP		SPB	
Substrate	Product	RT (min)	% Yield	RT (min)	% Yield	RT (min)	% Yield	RT (min)	% Yield	RT (min)	% Yield
(1a)	(2a)	50	70	120	70	150	70	160	65	180	70
(1b)	(2)	50	70	90	70	120	70	120	70	160	68
(1c)	(2c)	50	75	90	75	120	75	120	70	160	75

(1d)	(2d)	50	70	100	70	130	68	130	65	180	68
(1e)	(2e)	100	80	150	80	180	77	190	75	220	75
(1f)	(2f)	100	80	180	75	190	75	200	70	240	75
(1g)	(2g)	100	80	150	78	180	75	190	75	220	77
(1h)	(2h)	110	75	180	78	200	75	210	70	240	75
(1i)	(2i)	70	85	90	83	120	80	120	78	160	80
(1j)	(2j)	70	80	90	80	120	80	120	75	180	75
(1k)	(2k)	70	80	90	80	120	79	120	79	160	80
(1l)	(2l)	100	80	150	78	200	77	210	75	270	75
(1m)	(2m)	70	80	120	80	180	79	180	75	240	75
(1n)	(2n)	50	85	90	80	100	80	100	78	120	80
(1o)	(2o)	70	85	90	80	120	80	120	75	150	75
(1p)	(2p)	50	75	75	75	120	75	120	70	120	70
(1q)	(2q)	80	75	150	75	200	75	200	70	240	75
(1r)	(2r)	50	70	80	72	120	70	120	68	150	68
(1s)	(2s)	50	75	90	74	130	73	130	70	180	70
(1t)	(2t)	30	80	60	80	90	76	90	75	120	75

RESULTS AND DISCUSSION

Nitration of aromatic compounds using NaNO_2 in the presence of Peroxide reagent / KHSO_4 under acid-free conventional conditions

Potassium hydrogen sulfate (KHSO_4) is a reusable, green and efficient solid catalyst for various organic reactions. Heravi *et al* earlier accomplished that certain phenols and naphthols can be conveniently nitrated regioselectively with NaNO_2 using KHSO_4 as a catalyst in good yields.³⁸ The reaction times for most of the studied reactions are in the range of 5 to 7 hrs, depending on the structure of the substrate. In an effort to further enhance the reaction rates (i.e., further reduce the reaction times) we have used peroxy compounds (H_2O_2 , TBHP, PDS, PMS or SPB) as additives under conventional and non-conventional conditions under mineral acid-free medium. Spectroscopic data of isolated products are in agreement with our earlier reports.

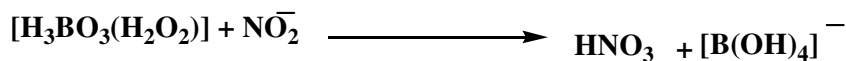


Scheme-1: Mono Nitration of Aromatic Compound using NaNO_2 in presence of KHSO_4 / Peroxide Reagent

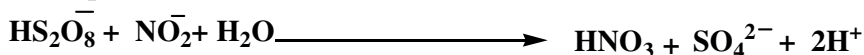
It is well known that the peroxy compounds (H_2O_2 , TBHP, PDS, PMS or SPB) form free-radical intermediates *in situ* during the course of several reactions. In order to detect the formation of free-radical intermediates pertaining to these peroxide reagents, olefinic monomers such as freshly prepared acrylamide or deaerated acrylonitrile were added to the reaction mixture under a nitrogen atmosphere. But the peroxy compounds (H_2O_2 , TBHP, PDS, PMS or SPB) used in this study did not initiate/induce

polymerization of added olefinic monomers even after 24 hrs under reflux conditions. This observation may indicate the absence of free radical intermediates. In the present study, KHSO_4 creates an acidic environment due to the protolysis of the bisulfate ion (HSO_4^-) followed by the release of a proton (H^+) without decomposition and thus acts as a pool of proton source.³⁶⁻³⁹ Basically, all the peroxy compounds in this study are strong oxidizing agents, which may present as free radical or ionic species. The absence of free radical species, thus suggests the participation of either the ionic species or molecular species in the mechanism of generating active nitronium ion ingredient as shown in the following steps:

Step-I: Generation of Nitronium ion electrophile



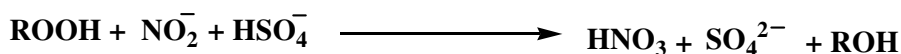
(SPB species)



(PDS species)

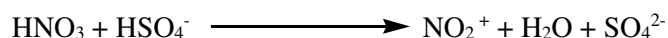


(PMS species)

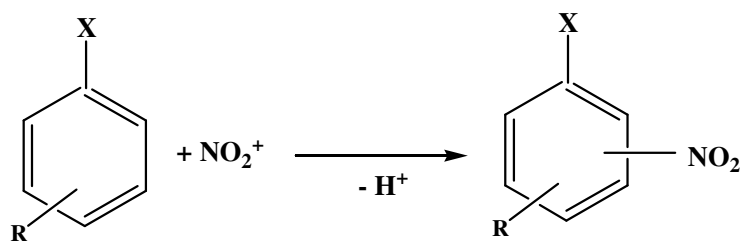


(Peroxide species; R= H for HP, tert- butyl for TBHP)

Active nitronium ion (NO_2^+) electrophile is then generated due to the reaction between HNO_3 and KHSO_4 according to the following reaction,



Step-II: Nitronium ion (NO_2^+) thus generated attacks the aromatic ring to afford nitroarene according to the following scheme-1,



(Where R = EDG or EWG; X= functional group)

Scheme-2

Table-4: Microwave assisted Nitration of Aromatic compounds using Peroxy compound/ $\text{NaNO}_2/\text{KHSO}_4$ under solvent-free conditions

Entry codes		PDS		PMS		H_2O_2		TBHP		SPB	
Substrate	Product	RT (sec)	% Yield	RT (sec)	% Yield	RT (sec)	% Yield	RT (sec)	% Yield	RT (sec)	% Yield
(1a)	(2a)	60	75	60	72	70	70	70	65	90	70
(1b)	(2)	40	75	40	70	50	70	60	70	70	70
(1c)	(2c)	40	80	40	78	50	75	60	72	70	75
(1d)	(2d)	40	75	40	73	50	70	60	70	75	70
(1e)	(2e)	50	82	70	80	80	79	85	75	90	75

(1f)	(2f)	60	80	80	77	90	75	95	72	100	75
(1g)	(2g)	50	80	70	80	80	78	85	75	90	78
(1h)	(2h)	60	75	80	78	100	75	110	72	120	75
(1i)	(2i)	40	87	50	85	60	82	65	80	65	82
(1j)	(2j)	45	82	60	80	65	80	70	75	75	75
(1k)	(2k)	40	85	50	83	60	80	65	80	65	82
(1l)	(2l)	100	82	140	80	160	78	180	75	180	78
(1m)	(2m)	50	85	55	82	60	80	70	78	90	80
(1n)	(2n)	30	88	40	85	45	82	50	80	60	80
(1o)	(2o)	50	88	60	85	65	80	65	80	70	80
(1p)	(2p)	30	80	40	80	45	78	50	75	60	75
(1q)	(2q)	60	80	70	75	80	75	90	75	120	75
(1r)	(2r)	40	75	50	74	60	73	60	70	60	70
(1s)	(2s)	40	75	45	77	50	75	50	70	60	72
(1t)	(2t)	30	85	40	85	45	80	45	80	55	82

The data presented in Tables-2 to 4 revealed that the reaction times (R.T) in microwave assisted (MWA) reactions reduced to a few seconds (30 to 50sec) from 2 to 7 hrs (under conventional methods), and 50 to 240 minutes with grindstone techniques at room temperature. Rate enhancements in MW assisted methods could be attributed to bulk activation of molecules because microwave irradiation directly supplements energy to all the reactant molecules present in the reaction vessel without heating the reactor as explained in earlier literature reports.⁵⁰⁻⁵³ On the other hand, rate accelerations under grindstone conditions could be explained due to bulk activation of the molecule due to the heat energy generated due to frictional forces operated during the course of grinding by pestle in a mortar⁴⁶⁻⁴⁹. Observed data further indicate that nitration followed o/p selectivity principle.

Spectral data of certain compounds:

- 1. 2-NO₂ Phenol:** ¹HNMR (300MHz, CDCl₃): δ 9.56 (s, 1H, OH), 8.19 (dd, 1H, J=9.1Hz, J=7Hz), 7.59 (s, 1H, J=8Hz J=7.5Hz) 6.99 (d, 1H, J=8.5Hz) 9.18 (d, 1H, J=8Hz); m/z = 139; Melting Point = 45-49°C
- 2. 2-Me- 4-NO₂ Phenol:** ¹HNMR (300MHz, CDCl₃): δ 10.55 (s, 1H, OH), 2.35 (s, 3H, Me), 6.85 (d, 1H, J=8.5Hz) 8.12 (d, 1H, J=8.5Hz) 8.25 (dd, 1H, J=8.5Hz, J=7.5Hz); m/z = 153; Melting Point = 95-98°C
- 3. 2-NO₂ 4-Me Phenol:** ¹HNMR (300MHz, CDCl₃): δ 10.42 (s, 1H, OH), 2.42 (s, 3H, Me), 7.32 (d, 1H, J=8Hz), 7.12(d, 1H, J=8Hz), 7.92(s, 1H); m/z = 153; Melting Point = 32-34°C
- 4. 3-Me- 4-NO₂ Phenol:** ¹HNMR (300MHz, CDCl₃): δ 10.64 (s, 1H, OH), 2.35 (s, 3H, Me), 6.85(d, 1H, J=8Hz), 8.12(d, 1H, J=8Hz), 6.76 (s, 1H); m/z = 153; Melting Point = 127-129°C
- 5. 4-NO₂ 2-Cl Phenol:** ¹HNMR (300MHz, CDCl₃): δ 10.66 (s, 1H, OH), 7.15(d, 1H, J=8.5Hz), 8.12(d, 1H, J=8.5Hz), 8.34(s, 1H); m/z = 174; Melting Point = 106-108°C
- 6. 2-NO₂ 4-Cl Phenol:** ¹HNMR (300MHz, CDCl₃): δ 10.54 (s, 1H, OH), 7.12 (d, 1H, J=8Hz), 7.82(d, 1H, J=8Hz), 8.36 (s, 1H); m/z = 174; Melting Point = 88-90°C

7. **2-NO₂ 4-Br Phenol:** ¹H NMR (300MHz, CDCl₃): δ 10.45 (s, 1H, OH), 7.10(d, 1H, J=8Hz), 7.72(d, 1H, J=8Hz), 8.25(s, 1H); m/z = 218; Melting Point = 92-96°C
8. **4-NH₂-2- NO₂ Phenol:** ¹H NMR (300 MHz, CDCl₃): δ 4.45 (s, 2H) 9.92 (s, 1H) 6.76 (d, J = 8Hz, 1H), 6.82 (d, J = 8Hz, 1H), 7.24 (s, 1H); m/z = 154; Melting Point = 125-128°
9. **4- NO₂ aniline:** ¹H NMR (300 MHz, CDCl₃): δ 7.94 (d, J = 5.5Hz, 2H), 6.76 (d, J = 5.49 Hz, 2H), 4.25 (brs, 2H); m/z = 138; Melting Point = 148-150°C
10. **2- NO₂-1-Naphthol:** ¹H NMR (300MHz, CDCl₃): δ 12.24(s, 1H, OH), 7.66(m, 1H), 7.76(m, 1H), 8.58(d, 1H, J=8.5Hz), 8.05(d, 1H, J=8.5Hz, J=4Hz), 8.15(d, 1H, J=8.5Hz), 7.44(d, 1H, J=9Hz); m/z = 189; Melting Point = 124-126°C
11. **1-NO₂-2-Naphthol:** ¹H NMR (300MHz, CDCl₃): δ 12.18(s, 1H, OH), 7.58 (m, 1H), 7.80 (m, 1H), 7.20(d, 1H, J=9Hz), 8.10(m, 1H), 7.68(dd, 1H, J=8.25Hz J=5Hz), 8.65(d, 1H, J=9Hz); m/z = 189; Melting Point = 98-100°C
12. **2- NO₂ furan:** ¹H NMR (300 MHz, CDCl₃): δ 6.68(dd, J=3.5Hz, J 1.75Hz, 1H), 7.34(dd, J=3.5Hz, J = 1.0Hz, 1H), 7.57(dd, J=1.75Hz, J = 1.0Hz, 1H); m/z = 113; Boiling Point = 85-88°C
13. **2- NO₂ thiophene:** ¹H NMR (300 MHz, CDCl₃): δ 7.07 (q, J = 4.25Hz, J = 5.25Hz, 1H), 7.55 (dd, J = 1.75Hz, J = 5.25 Hz, 1H), 7.93 (dd, J = 1.75Hz, J = 4.25Hz, 1H); m/z = 129; Melting Point = 44-47°C

CONCLUSION

The authors have accomplished peroxycompounds such as H₂O₂, peroxydisulfate (PDS), peroxymonosulfate (PMS), sodium perborate (SPB), and *tert*-butyl hydroperoxide (TBHP) as efficient catalysts for nitration of aromatic and heteroaromatic compounds in presence of NaNO₂/KHSO₄ under mineral acid free conventional and non-conventional methods such as microwave irradiation and grindstone techniques. Reaction times reduced from (2 to 7) hours to (25 to 60) minutes from conventional to grindstone method, which in turn reduced to (25 to 120) seconds in microwave assisted reactions. Product yields are also increased from 6 to 10% under microwave irradiation as compared to conventional procedures. All the synthesized compounds were characterized by ¹H NMR and mass spectral studies.

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