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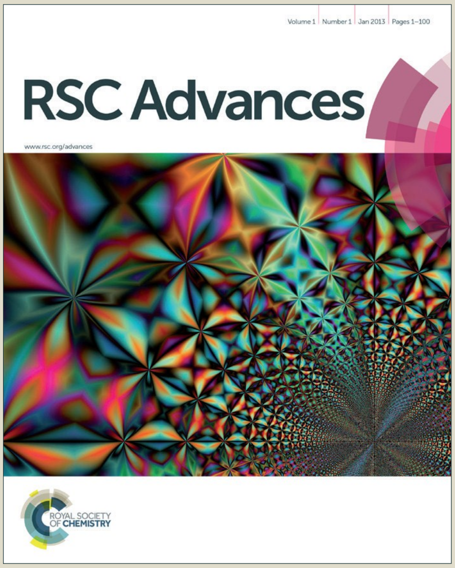

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ARTICLE TYPE

Nitration of arenes by 1-sulfopyridinium nitrate as an ionic liquid and reagent by in situ generation of NO_2

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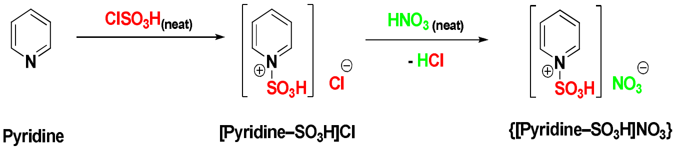
1-sulfopyridinium nitrate was synthesized as a potent nitrating agent for the nitration of arenes without the need for any co-catalysts. A variety of nitro compounds were synthesized and fully characterized by IR, ^{1}H NMR, ^{13}C NMR, thermal gravimetric analysis (TGA), differential thermal gravimetry (DTG), CHN analysis and mass spectroscopy. Mechanistically, *in situ* generated nitrogen dioxide as a radical from the reagent is proposed for the presented nitration protocol.

Nitro compounds are one of the principal group of compounds that have been widely used in organic chemistry and industry [1-5]. Nitro compounds hold many applications such as in high-energy materials, dyes, pharmaceuticals, perfumes, medicine and plastics and also play a significant role in the development of concept of mechanisms [6]. Therefore, high attention has been centered on the development of efficient and practical approaches for the synthesis of nitro compounds. The conventional nitration protocols are performed by the use of an excess of nitric acid or a mixture of nitric acid and sulfuric acid or dinitrogen pentoxide. As an alternative, yet efficient procedures, mixtures of nitric acid with aluminum chloride, polyphosphoric acid, perchloric acid, methanesulfonic acid, hydrogen fluoride and superacids such as boron trifluoride, triflic acid, fluorosulfonic acid and many others have been reported [7]. However, many of the reported approaches are associated with some drawbacks including: low yields, long reaction times, over nitration, the use of a large catalyst loading, low regioselectivity, oxidation of reagents and safety problems [8]. Therefore, designing an efficient nitration protocol is still of practical importance.

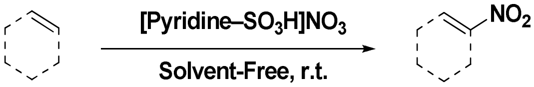
Recently, we reported sulfonic acid functionalized imidazolium salts (SAFIS) as a new class of acidic ionic liquids in which S–N bond has been formed leading to imidazole derivatives, as five-membered heterocyclic compounds. We found these materials have interesting applications as green and eco-friendly solvents, catalysts and reagents in organic transformations [8-23]. In continuation of our previous works, we also recently reported a new category of ionic liquids, namely sulfonic acid functionalized pyridinium salts (in which a S–N bond are formed in the pyridine ring leading to six membered heterocycles and used them as organocatalysts for the synthesis of bis(pyrazolil)methans [24], xanthene derivatives [25], bis(coumarin)methans [26] and hexahydroquinolines [27].

Having above facts and according to our previous work in the field of nitration [8], we were interested in the development of green chemistry protocols using new approaches such as the use of ionic liquids to reduce/eliminate co-catalysts and/or solvents. We prepared the ionic liquid 1-sulfopyridinium nitrate and found it is a highly efficient and green reagent without the need of a co-catalyst for the nitration of arenes and alkenes (Figure 1, Schemes 1 & 2).

Figure 1. The structure and color of [Pyridine–SO_3H]NO_3.



Scheme 1. Preparation of 1-sulfopyridinium nitrate {[Pyridine–SO_3H]NO_3}.



Scheme 2. Nitration of aromatic compounds using [Pyridine–SO_3H]NO_3.

1-sulfopyridinium chloride was synthesized by the reaction of pyridine with $ClSO_3H$ according to literature [24,25]. Then, by the reaction of [Pyridine–SO_3H]Cl with HNO_3, [Pyridine–SO_3H]NO_3 was prepared and characteized by IR, ^{1}H and ^{13}C NMR, mass spectroscopy as well as CHN analysis.

The IR spectrum of the reagent shows two strong peaks at about 1308 cm^{-1} and 1543 cm^{-1} which are typical of $\upsilon_{O-N=O}$ symmetric stretching vibration and $\upsilon_{O-N=O}$ asymmetric stretching vibration, respectively (Figure 2). Moreover, two peaks observed at 1183 cm^{-1} and 1334 cm^{-1} are related to vibrational modes of N–SO_2 and O–SO_2 bonds and a broad peak at 3100–3600 cm^{-1} could be signatures of O–H stretching of SO_3H group.

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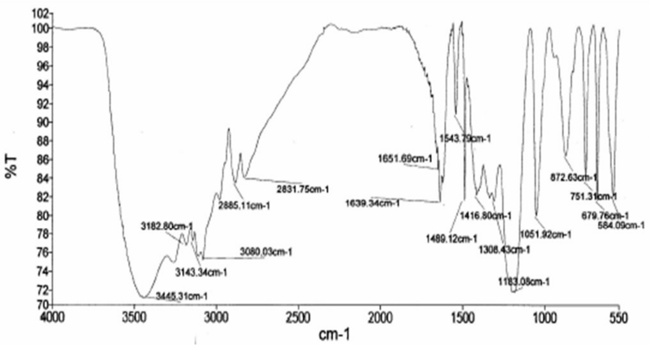


Figure 2. IR spectrum of 1-sulfopyridinium chloride {[Pyridine–SO_3H]NO_3}.

The ^{1}H NMR spectrum of [Pyridine–SO_3H]NO_3 shows the acidic hydrogen (SO_3H) peak at 11.37 ppm (Figure 2). To confirm that this peak is indeed related to the hydrogen of SO_3H in the compound, we also compared the ^{1}H NMR spectra of $ClSO_3H$, [$PySO_3H$]Cl and pyridinium chloride with HNO_3 in DMSO-d_6. In these spectra, the peaks of the acidic hydrogens of [Pyridine–SO_3H]NO_3, $ClSO_3H$, [Pyridine–SO_3H]Cl, pyridinium chloride and HNO_3 were observed at 11.37, 13.45, 13.96, 8.46, and 13.01 ppm, respectively (Figure 3) [8,24]. The mass spectrum of the compound gave the consistent molecular ion peak at 222 m/z.

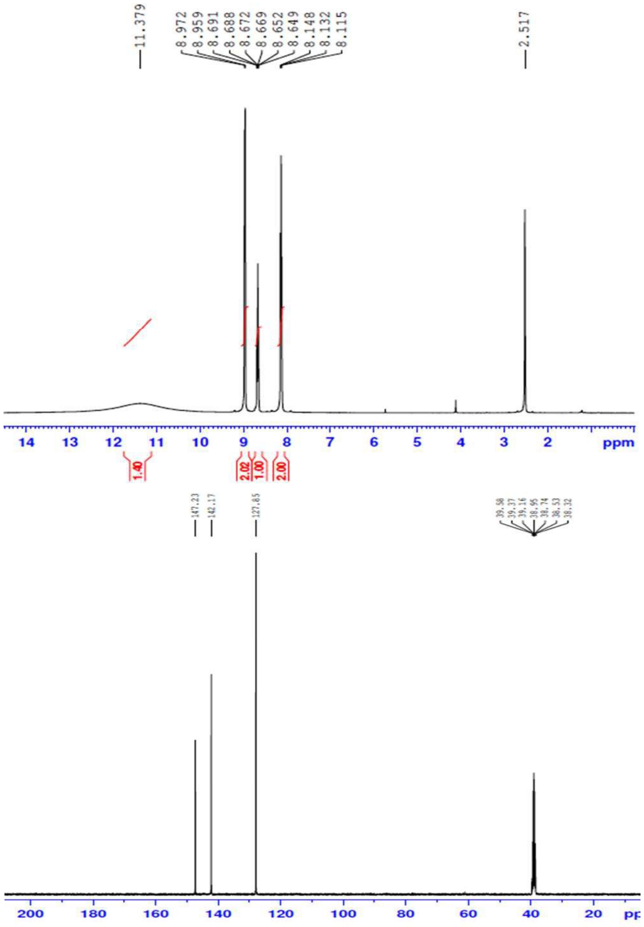


Figure 3. The ^{1}HNMR and ^{13}CNMR spectra of the 1-sulfopyridinium nitrate.

The thermogram (TG) of the reagent was studied and showed two main weight losses. The first loss of weight of the reagent was observed during the range of 60 ºC to 160 ºC, which could be related to loss of NO_2. The second weight loss occurred between 240 ºC and 320 ºC and the loss after 320 ºC is related to molecular decomposition (Figure 4).

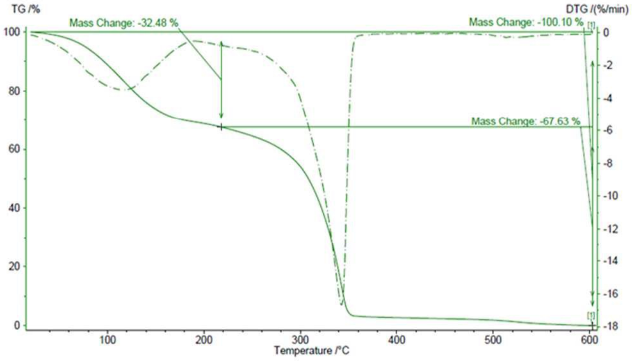
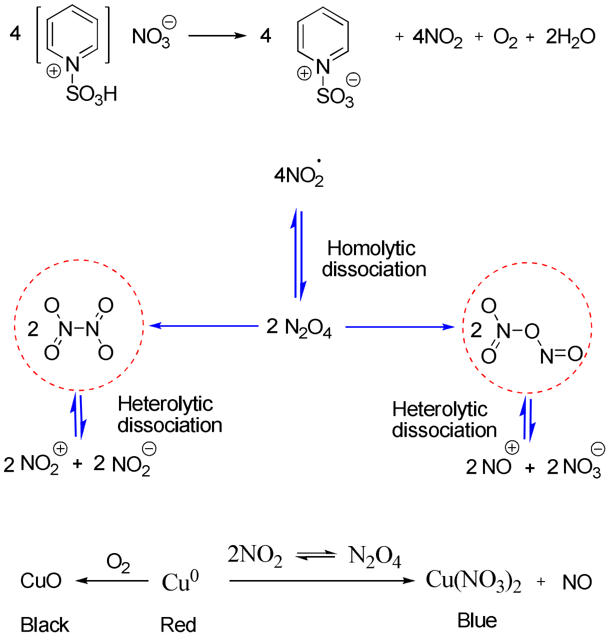


Figure 4. TG/DTG of the 1-sulfopyridinium nitrate.

In another experiment, the gas (nitrogen dioxide) that was released from [Pyridine–SO_3H]NO_3 upon heating at about 60°C was collected in a test tube, transferred to a round-bottomed flask in the presence of copper powder and ethyl acetate. NO_2 in equilibrium with dinitrogen tetroxide (N_2O_4)[28] reacts with copper metal to give $Cu(NO_3)_2$. In this reaction, appearance of the blue color due to copper nitrate formation in anhydrous media is a convincing evidence of the release of nitrogen dioxide (Figure 5) [8, 29]. Additionally, the excess copper powder residue turned black over time, suggesting that O_2 is produced from [Pyridine–SO_3H]NO_3 as well. Oxygen reacts with copper metal to form the black copper oxide as an insoluble residue (Scheme 3).



Scheme 3. The identification of nitrogen dioxide and oxygen using copper powder.

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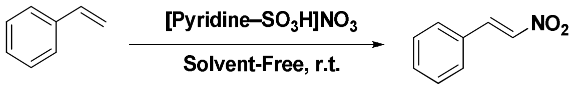
Figure 5. Preparation of copper nitrate (with blue color, right picture) from copper powder (left picture) as an evidence for the release of nitrogen dioxide.

A wide range of compounds including benzene, toluene, *o*-xylene, naphthalene, anthracene, phenols, anisol, 2-naphthol, anilines, styrene and bromobenzene were also nitrated with [Pyridine–SO$_3$H]Cl (**Table 1**). By the reaction of [Pyridine–SO$_3$H]NO$_3$ with benzenethiol and naphthalene-2-thiol the main products were 1,2-diphenyldisulfane and 1-(naphthalen-2-yl)-2-(naphthalen-6-yl) disulfane respectively. (Table 1, Entries 11 and 14) In this reaction conditions thiols were converted to the corresponding Ar-S• radical in the presence of NO$_2$. Two of these radicals dimerize to give diaryldisulfane and nitrous acid as a byproduct. Nitration of styrene as olefin compound was also studied and only the E isomer was obtained. 1-((E)-2-nitrovinyl)benzene was prepared in 62% yield after three minutes in presented reaction conditions. In our presented method, the regioselective nitration of styrene by 1-sulfopyridinium nitrate is more efficient in compared with previous literature reports (Scheme 4) [30].

Table 1. Nitration of Aromatic and aliphatic Compounds by Using {[Pyridine–SO$_3$H]NO$_3$.

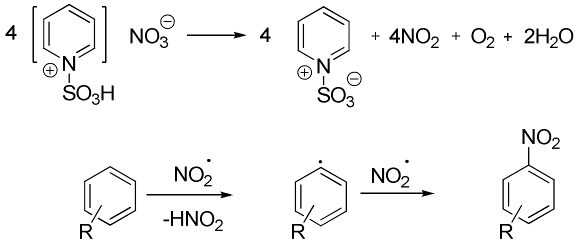
Product	Time (min)	Yield[a] (%)	m.p / b.p (˚C) [ref]
Nitrobenzene (1)	2	84	209-211 [31a]
4-nitrotoluene (2)	2	83	52-54 [31a]
2-nitrophenol (3a)	1	53	44-47 [32]
4-nitrophenol (3b)		35	114-116 [31a]
1-nitronaphtalene−2-ol (4)	immediately	92	101-103 [32]
4- chloro-2-nitrophenol (5)	2	78	83-85 [31b]
4-bromo-2-nitrophenol (6)	immediately	85	82-84 [31b]
1-nitronaphthalene (7)	immediately	82	58-61 [8]
9-nitroanthracene (8)	2	83	137-140 [33]
2-nitro4-benzyl phenol (9)	1	81	83-86
2-nitroaniline (10a)	immediately	45	71-73 [34]
4-nitroaniline (10b)		40	148-151 [35]
1,2-diphenyldisulfide (11)	2	83	62-65 [31a]
1-bromo 4-nitrobenzene (12)	2	80	122-124
1-(naphthalen-2-yl)-2-(naphthalen-6-yl)disulfane (13)	2	75	138-141
4-nitro anisol (14)	1	90	52-54 [31a]
1-((E)-2-nitrovinyl)benzene (15)	3	62	55-58 [30]

[a] Yield of purified product.



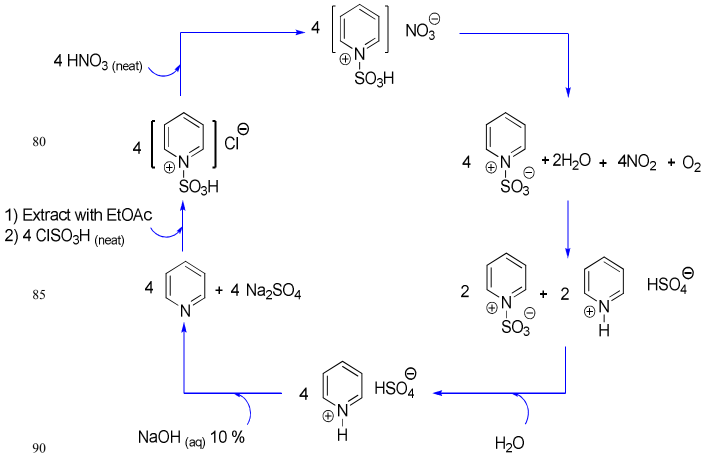
Scheme 4. Regioselective nitration of styrene.

In a proposed mechanism which is supported by literature [8], NO$_2$ gas released from [Pyridine–SO$_3$H]NO$_3$ reacts with aromatic compound to give the aromatic radical and nitrous acid (HNO$_2$). Second NO$_2$ radical and the aromatic radical react to yield nitro naphthalene (Scheme 5).



Scheme 5. The proposed mechanism for the nitration of aromatic compounds using [Pyridine–SO$_3$H]NO$_3$.

To investigate the regeneration of [Pyridine–SO$_3$H]NO$_3$, the reaction of 2-naphtol with reagent was carried out several times, and the resulting ionic liquid phases (unreacted [Pyridine–SO$_3$H]NO$_3$, the zwitterionic salt, and pyridinium salt) were combined. Water was added to the reaction mixture, and the reaction mixture was stirred for 5 min and then filtered. [Pyridine–SO$_3$H]NO$_3$ and zwitterionic salt is soluble in water and separated from the remained starting material and the product. [Pyridine–SO$_3$H]NO$_3$ and the zwitterionic salt were hydrolyzed in aqueous media. A solution of NaOH (10%) was then added to the reaction media, and the mixture was stirred for 5 min to give pyridine. The solution was extracted with ethyl acetate, washed with water, and dried. By the evaporation of the solvent, pyridine was separated (96% recovery). The recovered pyridine was reacted with chlorosulfonic acid to afford [Pyridine–SO$_3$H]NO$_3$. Then, [Pyridine–SO$_3$H]NO$_3$ reacted with nitric acid (100 %) to prepare [Pyridine–SO$_3$H]NO$_3$. The activity of the reproduced [Pyridine–SO$_3$H]NO$_3$ as nitration agent was almost identical to the original version (Scheme 6).



Scheme 6. Regeneration of [Pyridine–SO$_3$H]NO$_3$.

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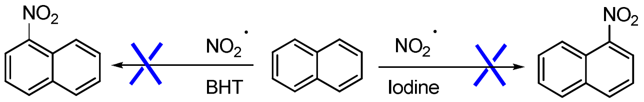
To compare the efficiency of the solution versus solvent-free conditions, a mixture of 2-naphtol (1 mmol) and [Pyridine–SO_3H]NO_3 (1 mmol) in some various solvents was investigated at room temprature. In the persence of several various solvents such as CH_2Cl_2, $CHCl_3$, EtOAc, EtOH and H_2O, the product was obtained in low yields (Table 2).

Table 2. Effect of various solvents on the reaction of 2-naphtol (1 mmol) with {[Pyridine–SO_3H]NO_3 (1 mmol) at room temprature.

Solvent	Time (min)	Yield[a]
EtOAC	60	65
$CHCl_3$	60	60
CH_2Cl_2	10	92
EtOH	60	25
H_2O	60	15

[a] Yield of purified product.

To confirm the existence of NO_2 radical in the reaction media, we studied the effective application of NO_2 with iodine or butylated hydroxytoluene (BHT) as a radical scavenger on a model reaction with naphthalene (Scheme 7) [36]. In the presence of iodine; the yield of 1-nitro naphthalene was very low even after 24 hours. Nitration of naphthalene was also tested using butylated hydroxytoluene (BHT) as a radical scavenger. In this reaction condition, nitration process was carried out slowly and the yield of 1-nitronaphthalene was decreased even after long reaction time due to major suppression of the active species in this reaction condition (Table 3).



Scheme 7. Trapping NO_2 Radical with Iodine and Butylated Hydroxytoluene (BHT).

Table 3. Effect of Iodine and butylated hydroxytoluene as radical scavengers on the nitration of naphthalene (1mmol) in the presence of {[Pyridine–SO_3H]NO_3 (1mmol)

Entry	Radical scavenger (mmol)	Time (min)	Yield[a] (%)
1	-	immediately	92
2	I_2 (0.3)	1440	35
3	I_2 (0.7)	1440	20
4	I_2 (1)	1440	10
5	BHT (0.3)	1440	45
6	BHT (0.7)	1440	35
7	BHT (1)	1440	20

[a] Yield of purified product.

To compare the efficiency of [Pyridine–SO_3H]NO_3 with the reported nitrating methods nitration of toluene was chosed. As Table 4 indicates that, [Pyridine–SO_3H]NO_3 has remarkably improved result compared with other methods shown in Table 4.

Table 4. Comparison of the results on the nitration of toluene using [Pyridine–SO_3H]NO_3 with those obtained by the recently reported methods.

Reaction Condition	Time (min)	Yield[a] (%)	Ref.
PVP-HNO_3 and PVP-H_2SO_4 CH_2Cl_2, r.t.	120	55	37
$Bi(NO_3)_3.5H_2O$ (1.5 equv) bmim (PF_6), 85 °C	90	39	38
$Bi(NO_3)_3.5H_2O$ (1.5 equv) 1,2-DCE, 85 °C	1380	50	38
[Msim] NO_3, CH_2Cl_2, r.t.	2	70	8
$VO(NO_3)_3$, CH_2Cl_2, r.t.	6	41	39
Toluene (1 mmol), $NaNO_2$ (1 mmol), CF_3CO_2H (34 mmol), r. t.	240	48	40
[Py–SO_3H]NO_3, solvent-free, r. t.	2	83	-[b]

[a] Isolated yield. [b] Our work.

Conclusions

Herein, we designed and synthesized the ionic liquid 1-sulfopyridinium nitrate [Pyridine–SO_3H]NO_3 as a new, a highly efficient and organic reagent without the need of a co-catalyst and solvent for the nitration of various aromatic compounds at room temperature.

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Experimental

2. Experimental

2.1. General

All chemicals were purchased from Merck or Fluka Chemical Companies. The known products were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by TLC using silica gel SIL G/UV 254 plates.

The ^1H NMR (400 or 300 MHz) and ^{13}C NMR (100 or 75 MHz) were recorded on a Bruker Avance DPX FT-NMR spectrometer (δ in ppm). Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. Thermogravimetric (TG) and differential thermal gravimetric (DTG) were analyzed by a Perkin Elmer (Model: Pyris 1). TG/DTG analysis (0 to 600 °C, temperature increase rate of 10 °C. min-1, nitrogen atmosphere).

2.2. General Procedure for the Preparation of the Ionic Liquid [Pyridine–SO_3H]NO_3.

A solution of pyridine (0.395 g, 5 mmol) in CH_2Cl_2 (40 mL) was added dropwise to a stirring solution of chlorosulfonic acid (0.58 g, 5 mmol) in dry CH_2Cl_2 (40 mL) over a period of 10 min at 0 °C. After the addition was completed, the reaction mixture was stirred for 20 min, stood and for 5 min, and the CH_2Cl_2 was decanted. Afterwards the liquid residue was triturated with CH_2Cl_2 (3× 10 mL), and dried under powerful vacuum at 90 °C to give [Pyridine–SO_3H]Cl as a viscous colorless oil in 95% yield

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(0.929 g) [24, 25]. Then, nitric acid 100% (0.315 g, 5 mmol) was dropwise added to [$PySO_3H$]Cl (0.993 g, 5 mmol) over a period of 5 min at room temperature under a continuous flow of nitrogen to remove the HCl gas that is produced. The resulting mixture was stirred for 10 min under these conditions to give [Pyridine–SO_3H]NO_3 as a viscous yellow red oil in 97% yield.

1-sulfopyridinium nitrate. Yellow Red oil; IR (Nujol) cm^{-1}; 1183, 1308, 1543, 3100-3600; ^1H NMR (300 MHz, DMSO-d_6) δ (ppm) 8.11-8.14 (t, $J = 9$ Hz, 2H), 8.64-8.69 (m,1H), 8.95-8.97 (d, $J = 6$ Hz, 2H), 11.37 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) 127.85, 142.17, 147.23. Anal. Calcd (%) for $C_5H_6N_2O_6$: C, 25.03; H, 3.36; N, 11.66; S, 13.35. Found: C, 24.22; H, 3.115; N, 11.95 ; S, 13.51.

2.3. General Procedure for the Nitration of Compounds.

To a round-bottomed flask (10 mL) was added [Pyridine–SO_3H]NO_3 (0.222 g, 1 mmol). The aromatic compound (1 mmol) was then added, and the mixture was stirred at room temperature. After the reaction was completed (monitored with TLC), dichloromethane (5 mL) was added to the reaction mixture, and the mixture was stirred for 2 min and separated. The organic solvent was evaporated, and the product was easily purified by short column chromatography. Note: For the nitration of aniline, after the reaction was completed, the reaction mixture was basified to pH 8 by the slow addition of 10% NaOH solution. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic solution was washed with brine, dried over $MgSO_4$, filtered, and concentrated to give a crude product, which was purified with short column chromatography.

Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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Graphical Abstract

Nitration of arenes by 1-sulfopyridinium nitrate as an ionic liquid and reagent by *in situ* generation of NO_2

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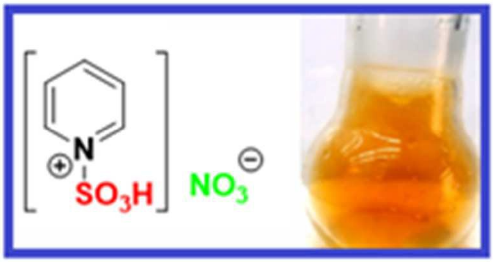

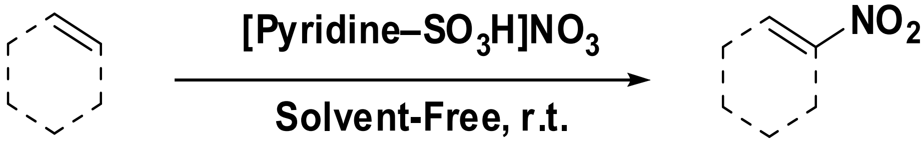

1-sulfopyridinium nitrate was synthesized as a potent nitrating agent for the nitration of arenes without the need for any co-catalysts.