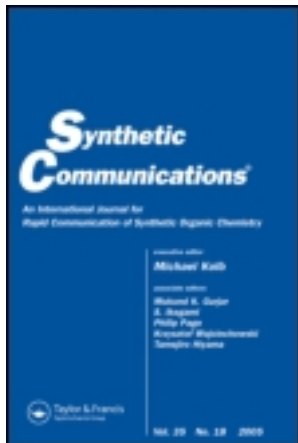


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AMMONIUM NICKEL SULPHATE MEDIATED NITRATION OF AROMATIC COMPOUNDS WITH NITRIC ACID

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ABSTRACT

Aromatic compounds were efficiently nitrated under mild conditions employing ammonium nickel sulphate and nitric acid as a reagent. This procedure works efficiently at room temperature yielding mononitro derivative in fair to good yield with high regioselectivity.

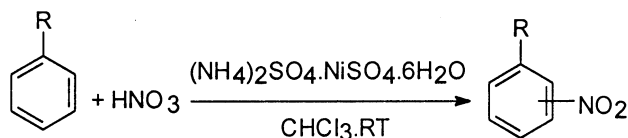
Nitration of aromatic compounds is an important industrial process.^{1–4} The nitroaromatic compounds so produced are widely utilized for the synthesis of dyes, pharmaceuticals, perfumes, and plastics. Usually the nitration of aromatic compounds is catalyzed by concentrated

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strong acids.⁵⁻⁹ Unfortunately, nitrations of aromatic compounds typically require a mixture of concentrated fuming nitric acid with sulfuric acid, leading to excessive acid waste. Alternatively, nitration of aromatic compounds has been studied by various nitrating agents under different conditions.¹⁰⁻¹⁵ Among these, most of the methods have some drawbacks, such as regioselectivity, over-nitration, and competitive oxidation of substrates.¹⁶⁻¹⁸ Therefore, there is still a need for the development of new methods for the nitration of aromatic compounds.

For a long time nitric acid has been used as such or with other reagents for the nitration of aromatic compounds.¹⁹⁻²¹ Recently, we have reported that ammonium molybdate and nitric acid can act as good catalysts for the nitration of aromatic compounds under reflux conditions, giving the corresponding nitro derivatives in good yields with high selectivity.²²⁻²⁴ The results obtained in our earlier investigation prompted us to search for more efficient and operationally simple catalysts. In view of this, it was thought worthwhile to use a metal complex or salt in combination with nitric acid for nitration of aromatic compounds with a hope (a) to increase the rate and yield of the reactions; (b) to improve ortho/para ratio of the nitrated aromatic compounds; and (c) to run the reactions under nonaqueous conditions.

Ammonium nickel sulphate was selected as the most promising candidate for the proposed nitration reactions. Accordingly, a range of aromatic compounds were treated with 1 equiv. of 69% nitric acid in chloroform at room temperature in the presence of 1 equiv. of ammonium nickel sulfate (Scheme). The results are shown in Table 1. Dinitrated products were not observed in any case. In the case of benzene, nitration did not take place even after 24 h under reflux. However, chlorobenzene underwent nitration smoothly, probably because of the presence of an activating chloro group.



Scheme.

Nitration of aromatic compounds in the presence of ammonium nickel sulfate proceeds rapidly, affording high yields (85–95%) of the corresponding mononitro derivatives with high regioselectivity. In the absence of catalyst, a sluggish reaction occurred and the yield of nitrated product was less than 20%. Progress of the reaction is monitored by a visible

Table 1. Nitration of Aromatic Compounds in the Presence of Ammonium Nickel Sulfate $(\text{NH}_4)_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$

Entry No.	Substrate	Reaction Time/h	Yield %	
			Para	Ortho
1	Phenol	3	85	15
2	<i>o</i> -aminophenol	3	92	—
3	<i>p</i> -chlorophenol	4	—	94
4	<i>p</i> -nitrophenol	4	—	92
5	<i>p</i> -cresol	3	—	93
6	Acetanilide	4	86	14
7	<i>o</i> -chloroacetanilide	3	93	—
8	<i>p</i> -nitroacetanilide	3	—	94
9	<i>p</i> -chloroacetanilide	3	—	93
10	<i>p</i> -bromoacetanilide	3	—	94
11	Benzanilide	4	84	16
12	<i>p</i> -nitrobenzanilide	3	—	92
13	<i>p</i> -chlorobenzanilide	3	—	94
14	Aniline	4	88	12
15	<i>p</i> -nitroaniline	3	—	93
16	<i>p</i> -chloroaniline	3	—	92
17	<i>o</i> -ethylaniline	3	93	—
18	<i>p</i> -anisidine	3	—	90
19	Chlorobenzene	3	86	14
20	Toluene	4	88	12

change in the color of the reaction mixture and also from TLC during the course of reaction. To check the generality of the reaction, it is carried out with naphthalene, anthracene to give α -nitronaphthalene (85%) and 9-nitro anthracene (95%), respectively, which proved to be quite satisfactory. The regioselectivity was higher compared with those observed for classical nitration.

To shed light on the reaction mechanism, further work is in progress. However, based on the results obtained so far, it is believed that the reaction occurred by nitronium ion-bound metal species, which is thought to be a key intermediate. The nitrated products were characterized by comparison of their spectral and physical data with authentic samples. The ratio of *o*- and *p*-products was determined by HPLC and isolated by chromatography.

The foregoing results thus substantiate a new, mild, operationally simple, and efficient method for the nitration of aromatic compounds using ammonium nickel sulfate resulting in corresponding nitro derivatives

in fair to good yield with high regioselectivity. Therefore, the present method is believed to be a good method for the synthesis of nitro compounds in organic synthesis.

EXPERIMENTAL

All chemicals and solvents were obtained from commercial sources and used without further purification. $^1\text{H NMR}$ were recorded are 90 MHz in CDCl_3 solvent. IR spectra were obtained on G.C. FTIR using a Vartan Nicolet USA apparatus. EI mass spectra were determined by using a V.G. Micromass 7070 and Finnigan mal 1020 apparatus. Melting points were determined on a Veego digital automatic melting point apparatus and are uncorrected.

Typical Procedure

The following procedure is a representative reaction. Phenol (0.094 mL, 1 mmol) and ammonium nickel sulfate (394 mg, 1 mmol) were taken in chloroform (10 mL). Then 69% HNO_3 (0.063 mL, 1 mmol) was added and the reaction mixture was stirred at room temperature for 3 h. After the completion of the reaction as indicated by TLC, the reaction mixture was filtered off and washed with water, the organic layer was separated out, dried over sodium sulfate, and evaporated under vacuum. The crude product (yield 92%) was purified by silica gel (100–200 mesh) chromatography using ethyl acetate : hexane (3:7) as eluent to get *p*-nitrophenol (108 mg 85%) m.p. 113°C (lit. m.p. 114°C) and *o*-nitrophenol (19 mg 15%) m.p. $44^\circ\text{--}45^\circ\text{C}$ (lit. m.p. 45°C).

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