

# Nitration of Phenolic Compounds with Magnesium nitrate and acetic acid

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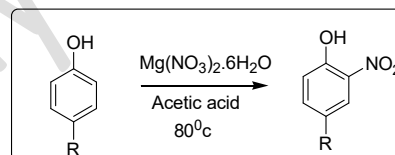
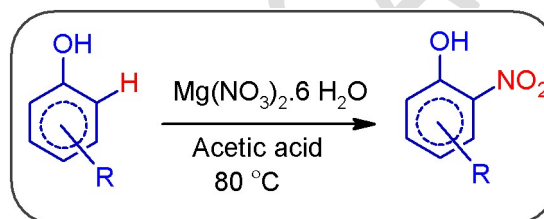
## Abstract

Nitration of aromatic compounds is an indispensable reaction for organic chemists. Various metal nitrates are being used now-a-days as an eco-friendly nitrating agent instead of harsh strong acids, namely, nitric and sulfuric acids. A mixture of calcium nitrate and acetic acid, as well as a mixture of magnesium nitrate and alumina sulfuric acid, are reported to be used as nitrating agent. Inferring from these ideas, a mixture of magnesium nitrate and acetic acid (glacial or about 80% aqueous) is introduced for the first time as a fairly efficient nitrating agent for phenolic compounds successfully.

**Keywords:** Nitration, phenolic compound, eco-friendly

## 1. Introduction

Nitration of aromatic compounds is an elementary reaction having significant industrial importance. A mixture of concentrated or fuming nitric acid with sulfuric acid is commonly used as a nitrating reagent for the nitration of aromatic compounds.<sup>1</sup> However, this may lead to easy oxidation of highly reactive aromatic compounds, such as phenols and anilines. In a search of eco-friendly nitration reaction that does not require strong acids such as nitric and sulfuric acids, the use of various metal nitrates are proposed.<sup>2</sup> However, most of these methods involve the use of metal nitrates deposited on clay (Claycop: copper nitrate on montmorillonite clay; clayfen: ferric nitrate on clay; clayzin: zinc nitrate on clay; etc.) for nitration of electron- rich aromatic compounds.<sup>3</sup> The clay derivatives prepared by Laszlo et al. follows a lengthy experimental procedure. The nitration process requires the use of chlorinated solvents for the reaction and solvent extraction of the product from clay, and thus lead to a substantial amount of chemical waste. During literature survey it has been found that calcium nitrate and acetic acid as an efficient nitrating agent<sup>4</sup> as well as magnesium nitrate and alumina sulfuric acid<sup>5</sup> are also useful for similar reaction. In search of a novel and safe method of nitration, mixing these ideas, it has been found that magnesium nitrate and acetic acid (glacial or about 80% aqueous) can serve as a fairly efficient nitrating agent for phenolic compounds.



**Figure 1:** General reaction of phenolic compound with mixture of magnesium nitrate and acetic acid

## 2. Experimental

Melting points are uncorrected.

### General nitration procedure with magnesium nitrate:

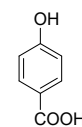
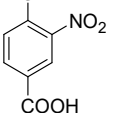
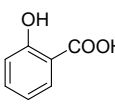
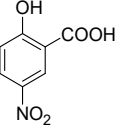
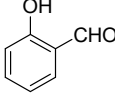
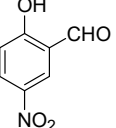
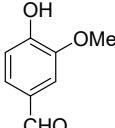
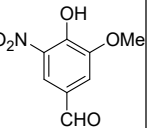
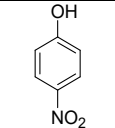
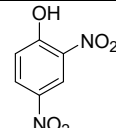
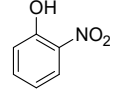
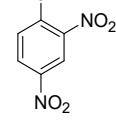
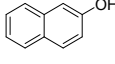
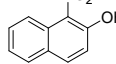
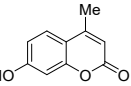
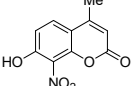
Magnesium nitrate (1equiv.) was dissolved in warm acetic acid and phenolic compound (0.3 equiv) was added to it. Then the mixture was heated in an oil bath at above 80°C for 5 min. Phenolic compound was dissolved completely and the solution became dark. It was immediately poured into ice cold water. The resultant turbid dark colored solution was placed in a refrigerator. After few hours, yellow crystals that separated, was filtered, washed with ice cold water and dried. M.P was noted, matched with literature data and <sup>1</sup>H NMR of few samples were done.

## 3. Result and discussion:

A simplified experimental procedure is opted for as stated hereby. The reaction of 1 gm of phenolic compound mixed with 3 gm of magnesium nitrate and 7 mL of glacial acetic acid heated for 5 min in water bath shows the

complete disappearance of the starting phenol. The reaction mixture is then poured into cold water and stored for some time in a refrigerator. The yellow crystals that separated are washed free of acid with water and then allowed for air dry. The melting point of the recrystallized product indicated it to be a mono-nitro compound; the yield is found to be around 42-65% depending on the substrates. Similar experiments are performed with eight different phenols which also lead to mono-nitro compounds. The details of the substrates, products and yields are presented in Table-1.

**Table 1:** Substrates and corresponding products of nitration reaction with mixture of magnesium nitrate and acetic acid

Entry	Substrate	Product	Yield (%)	M.P. (°C)	Lit. M.P (°C)
1			50	182	184 <sup>b</sup>
2			45	233	235 <sup>b</sup>
3			47	129	128 <sup>b</sup>
4			63	172	175 <sup>f</sup>
5			42	110	107-110 <sup>6</sup>
6			45	108	107-110 <sup>6</sup>
7			60	100	103 <sup>6a</sup>
8			65	Above 200	255 <sup>b</sup>

In all the cases mono-nitro compounds are obtained. Nitration of coumarin compound, in general, gives mixture of 6-nitro and 8-nitro products during nitration with

mixed acid. However, in this experimentation exclusively 8-nitro product is obtained. Further, this method is found to be successful only with various phenols but failed in case of amines.

## 4. Conclusions

An efficient eco-friendly nitration method of phenols with magnesium nitrate as the nitrating agent in the presence of glacial acetic acid is developed. The method offers numerous advantages in terms of simple experimental procedure, cheap reagents and hence, it is a useful addition to the existing methods which is compatible with the requirements of green chemistry.

## 5. Acknowledgements

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## 6. Notes and References

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