Microwave-Assisted Synthesis of Para-Nitrophenol Using Calcium Nitrate

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ABSTRACT

Conventional process of nitrating phenolic compounds involves the use of excess corrosive reagents that impose environmental threats. Rapid and environmentally friendly microwave-assisted nitration of phenol has been employed to limit the use of corrosive nitric acid and sulfuric acid. In this study, phenol is reacted to calcium nitrate and acetic acid, which served as nitrating agents. The solution is irradiated under microwave to complete the nitration process. This microwave-assisted-synthesis is a rate-enhanced process that showed complete nitration in a short reaction time of 1 min with a high yield of 89%. Bands of phenyl ring, OH, CO, and nitro groups observed in the FTIR spectra correspond to the vibration modes of para-nitrophenol. GCMS analysis showed a retention time of 7 min for the product with 139m/z base peak with matches that confirms the synthesis of para-nitrophenol. This microwave-assisted method can be employed as an efficient, environmentally safe, and rapid alternative nitration method for the synthesis of para-nitrophenol.

Keywords: Microwave-assisted, Nitration, para-Nitrophenol, Nitrating agents.

INTRODUCTION

Para-nitrophenol or 4-nitrophenol belongs to the group of phenolic compounds where a nitro group is opposite the hydroxy group in the benzene ring. Among the various applications of 4-nitrophenol are its use in the pharmaceutical industry as an intermediate in paracetamol synthesis and as precursors for phenetidine and acetophenetidine1. It is also synthesized for its application in dye and pigment production as well as in plastics formulation and polymer engineering2. Manufacturer of agrochemical products use para-nitrophenol as a raw material in fungicides and is an evident degradation product of pesticides such as parathion and fluoridifen3,4,5.

Nitrophenols are not naturally occurring and hence are synthetically synthesized for a variety of uses. Traditional methods of synthesis follow the mechanism of nitration of aromatic compounds, which uses liquid mixtures of nitric acid and sulfuric

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acid. Traditional synthesis yields a mixture of ortho- and para-nitrophenols due to the low regioselectivity of the method. Another drawback is the production of acid wastes from the excessive use of strong acid reagents. Alternative nitration procedures were also established to lessen the production of acid wastes and to enhance the regioselectivity of the reaction. The use of metal catalysts and molecular frameworks such as zeolites, clayfen, claycop and clayzic, metal nitrates, and solvent-free reactions were being explored as possible procedures towards green chemistry and regioselectivity of the nitration reaction. Another method is the microwave-promoted nitration, which uses nitrate salts, less corrosive acids, proceeds by a rapid reaction time, with recorded high regioselectivity and higher product yield.

In this study, phenol was nitrated to yield para-nitrophenol. The nitration process was carried out in a microwave-assisted set-up using calcium nitrate and acetic acid as nitrating agents. This nitration method was completed in a minute with the use of commonly available reagents that are less toxic and less corrosive compared to the traditional method.

MATERIALS AND METHODS

Reagents and Instruments
Reagents used in this study, including phenol, calcium nitrate, glacial acetic acid, and methanol, are all reagent grades. A Gas Chromatography-Mass Spectrometry (GC-MS) TQ4080 (Shimadzu) and a Spectrum Two FT-IR Spectrometer (PerkinElmer) were used to characterize the synthesized product.

Microwave-assisted Nitration
The microwave-assisted synthesis of nitrophenol was based on literature with modifications. Briefly, 1.0 mL phenol, 2.0 g Calcium nitrate, and 5.0 mL glacial acetic acid were stirred in an Erlenmeyer flask. The mixture was covered and placed at the center of a microwave model MWP305ES with 900W output at 2450MHz. The microwave-assisted nitration reaction was carried out by irradiating the reaction mixture for 1 minute. A darkening of the mixture was observed after the reaction was complete. This was then allowed to cool and refrigerated prior to characterization experiments.

FTIR Characterization
The reaction product was analyzed under FTIR to confirm the presence of nitrophenol.

RESULTS AND DISCUSSION

Synthesis and FTIR Characterization
This study employed the use of microwave irradiation instead of the traditional process, which involves heating under reflux. This technique is found to be useful in the nitration process as the reaction proceeded at a much faster rate decreasing the reaction time from hours to just minutes. The mechanism of nitration of aromatic compounds proceeds by an electrophilic attack involving nitronium ion. Here, commonly available and environment-friendly reagents were used as nitrating agents instead of the corrosive nitric acid and sulfuric acid used in conventional nitration. Calcium nitrate reacted with acetic acid to yield calcium acetate and nitric acid, which served as the source of the nitronium ion. This then reacted with the aromatic ring of phenol and yielded the nitrophenol product with 89% yield.

The collected product was analyzed under FTIR to confirm the presence of nitrophenol.
The IR spectrum of the product in Fig. 1 showed IR peaks representing the nitro, OH, and CO groups and a phenyl ring, which are all attributes of the nitrophenol product. Corresponding frequencies to the different vibration modes of the IR bands are listed in Table 1.

Table 1: Summary of the vibration modes and corresponding IR frequencies for p-nitrophenol

| Frequency, cm$^{-1}$ | Vibration Mode                                    |
|---------------------|---------------------------------------------------|
| 627                 | Scissoring NO$_2$ + in-plane CH ring vib          |
| 755                 | Wagging NO$_2$                                    |
| 764, 885            | NO$_2$ + out-of-plane CH vib                      |
| 1387, 1550          | NO$_2$ Symmetrical + asymmetrical stretch         |
| 692                 | OH torsional vib                                  |
| 1169                | OH in-plane bend                                  |
| 3046-3620           | OH stretch                                        |
| 1232-1279           | CO stretch                                        |
| 1112, 1167, 1305, 14747 | CH bend                        |
| 1009                | Ring breathing vib                                |
| 1636                | C=C aromatic ring vib                            |

The band at 627 cm$^{-1}$ corresponds to the NO$_2$ scissoring and in-plane ring vibrations. Bands at 755 cm$^{-1}$ (wagging), 764 and 885 cm$^{-1}$ (out of plane vibration), and 1387 cm$^{-1}$ and 1550 cm$^{-1}$ (symmetric and asymmetric stretching) all correspond to the NO$_2$ vibration modes. Band at 3046-3620 cm$^{-1}$ corresponding to OH stretching frequencies was observed. At 1169 cm$^{-1}$ and 692 cm$^{-1}$, OH in-plane bending and torsional vibrations were noted, respectively. The CO stretch in the phenyl ring is observed as a strong IR band at 1232-1279 cm$^{-1}$. The rest of the phenyl ring vibrations tend to be independent of the nature of the aromatic ring substituents compared to the previously noted IR bands and frequencies.$^{14}$ These vibrations are the C-H bending at 1112 cm$^{-1}$, 1167 cm$^{-1}$, 1305 cm$^{-1}$, and 1474 cm$^{-1}$, the ring breathing vibration at 1009 cm$^{-1}$ and C=C aromatic ring vibration noted at 1636 cm$^{-1}$.

GC-MS Characterization

The collected sample was prepared for gas chromatography analysis without further derivatization. The chromatogram showed in Fig. 2 with the peak of the product at a retention time of 7.0 min, without the need for further derivatization of the sample. A good elution of the sample from the column is notable without the derivatization process as most studies require methylation$^{15}$ and silylation$^{16}$ as derivatization steps prior to GC analysis. The detector used was MS, which showed the spectra of the fragmentation of the product. Matches with the library of compounds confirm the product to be 4-nitrophenol with a 139 m/z ratio shown in Figure 2.

![Fig. 2. GC-MS Chromatogram of p-Nitrophenol](image)
CONCLUSION

This current study demonstrates a fast microwave-assisted nitration process to synthesize para-nitrophenol. The presented method follows a rapid reaction with the use of common reagents that are less toxic and less corrosive compared to the traditional nitration reaction. The procedure gives a high yield with high regioselectivity to para-nitrophenol as supported by the FTIR and GCMS characterizations. This can serve as an efficient, eco-friendly and rate-enhanced method for the small-scale preparation of para-nitrophenol.

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Conflict of Interest

The authors declare that there is no conflict of interest in this work with regard to publication.

REFERENCES

1. Abdollahi, M.; Mohammadirad, A. Encyclopedia of Toxicology., 2014, 575-577.
2. Bhatti, Z. I.; Toda, H.; Furukawa, K. Water Research., 2002, 1135-1142.
3. Tian, J.; An, X.; Liu, J.; Zhao, R.; Wang, J.; Chen, L. Journal of Environmental Engineering., 2018.
4. Bae, S.; Gim, S.; Kim, H.; Hanna, K. Appl. Catal., 2016, 541-546.
5. Chen, X.; Murugananthan, M.; Zhang, Y. Chem. Eng. J., 2016, 1357-1365.
6. Clark, J. H.; Macquarrie, D. J. Organic Process Research and Development, 1997, 149-162.
7. Esakkidurai, T.; Pitchumani, K. J. Molecular Catalysis A: Chemical, 2002, 305-309.
8. Laszlo, P.; Pennetreau, P.I. Org. Chem., 1987, 2407-2410.
9. Muathen, H. A. Molecules., 2003, 593-598.
10. Kumar, A.; Sharma, S. Green Chemistry., 2011, 2017-2020.
11. Bose, A. K.; Ganguly, S. N.; Manhas, M. S.; Rao, S.; Speck, J.; Pekelny, U.; Pombo-Villars, E. Tetrahedron Letters., 2006, 1885-1888.
12. Sana, S.; Reddy, K.; Rajanna, K.; Venkateswarlu, M.; Ali, M. International Journal of Organic Chemistry., 2012, 233-247.
13. Yadav, U., Mande, H.; Ghalsasi, P. Journal of Chemical Education., 2012, 268-270.
14. Abkowicz-Bienko, A. J.; Latajka, Z.; Bienko, D. C.; Michalska, D. Chemical Physics., 1999, 123-129.
15. Noya, Y.; Mikami, Y.; Taneda, S.; Mori, Y.; Suzuki, A. K.; Okura, K.; Seki, K. Environ. Sci. Pollut. Res., 2008, 318-321.
16. WenJue, Z.; DongHong, W.; XiaoWei, X.; BingYi, W.; Qian, L.; Satyanarayanan, S.; & ZiJian, W. Chinese Science Bulletin., 2011, 275-284.