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MICROWAVE-INDUCED BISMUTH NITRATE-IMPREGNATED CLAY-MEDIATED NOVEL DINITRATION OF 9,10- DIHYDROPHENANTHRENE: A PRECURSOR FOR NEW HETEROCYCLES

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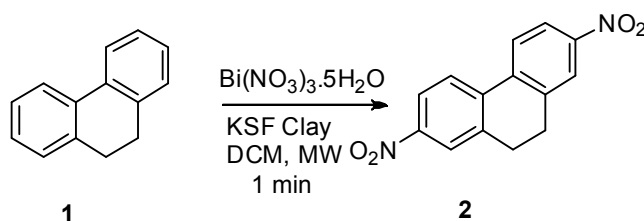
Abstract: A facile method for the dinitration of 9, 10-dihydrophenanthrene using domestic microwave-induced bismuth nitrate-impregnated clay is developed

Introduction:

Microwave-induced organic reactions have been widely used in synthetic organic chemistry. Despite the advantages of using automated microwave oven, we find domestic microwave oven can be much superior when undergraduate chemistry demonstration is pursued. Automated microwave oven is extremely expensive and it is difficult to have this type of microwave oven in teaching undergraduate research courses. In addition, it is understandable that a single automated microwave oven is not sufficiently enough to demonstrate reactions to undergraduates who do not have adequate time for research because of their many other course assignments. However, it is crucial for the undergraduates to have research experience. Undergraduates who have participated in laboratory-based research prove to become more successful in their future career development. Our research groups have been engaged in research with numerous undergraduates. Therefore, we always seek procedures that undergraduates can perform with success within the allocated time. The chemistry developed by our undergraduates were instrumental not only for their successes, but also some of these methods were competitive enough for external funding. On this basis, method described herein is not restricted to undergraduates only.

Results:

In this paper, we report an extremely facile dinitration of dihydrophenanthrene using a combination of bismuth nitrate impregnated with clay and microwave irradiation¹. Aromatic nitration is one of the most crucial reactions. This reaction requires concentrated nitric acid/sulfuric acid mixture or nitronium tetrafluoroborate.² It is understandable that these reagents are highly corrosive. To overcome the shortcoming of nitric acid method, we reported aromatic nitration with bismuth nitrate impregnated with clay. Bismuth nitrate is a crystalline non-toxic solid and highly economical salt. A number of aromatic compounds was nitrated very efficiently using this method.³⁻⁴ For example, anisole, phenol, toluene, eugenol, naphthalene, anthracene, phenanthrene and chrysene produced nitro derivatives at room temperature. Realizing the importance of this method, we have performed nitration of dihydrophenanthrene and unexpected products have been formed under identical conditions. Microwave irradiation of the solid mass of 9, 10-dihydrophenanthrene impregnated with clay and bismuth nitrate for 4-5 minutes afforded 3,6-dinitro-9,10-dihydrophenanthrene in excellent yields. In contrast to all our previous reactions, this is the only reaction in which a dinitro derivative of an important aromatic compound is produced. This reaction is very fascinating because of a number of reasons. For instance, upon prolonged exposure with bismuth nitrate the benzylic methylene groups of this compound could oxidize to alcohols or ketones. The alcohols could further undergo dehydration to alkenes. A diketo system could be further cleaved to diacids under these reaction conditions. Interestingly, no side reactions as mentioned above actually take place. Despite the presence of two benzylic methylenes and symmetrical structure of dihydrophenanthrene, we have isolated a single dinitro compound in excellent yield. (**Scheme1**).



The reaction optimization are delineated in table1.

Table: Optimization of Bismuth nitrate catalyzed Nitration of 9, 10-Dihydrophenanthren (DHP)

Entry	Methods	Solid Support	Time (minutes)	Temp.	Yield (%)
1	Microwave	Silica gel	3	50	55
2	Microwave	MS(4A ⁰) Powder	2	50	45
3	Microwave	Alumina (acidic)	3	50	60
4	Microwave	KSF Clay	1	50	90

The above reaction was repeated by many undergraduates to confirm the validity of the results. All students performed the reactions was able perform the reaction, extract the reaction mixtures, evaporate the solvents and record the NMR data within 2 hour starting from the beginning of the experiment. The successful preparation of dinitro derivative as described herein has become very important for the students since they learn to use a relatively complex aromatic hydrocarbon, Symmetry/asymmetry present in the molecule, surface-mediated reaction, use of non-toxic reagent as an alternative of corrosive reagents, extraction of a reaction mixture, follow up a reaction mixture through TLC and finally identify the structure of the product by NMR and IR. The absence of keto group can be

confirmed by IR and NMR spectra. This method and compound is very useful for our research on the synthesis of novel beta-lactams and polyaromatic compounds as anticancer agents⁵. The 3,6-dinitro-9,10-dihydrophenanthrene is highly functionalized to produce a number of crucial compounds that may demonstrate anticancer properties. For example, the dinitro compound can be reduced to diamines and these diamines can be converted to anticancer agents following our own methods.^{5,6}

The results obtained from this study is crucial because chrysene, a symmetrical aromatic hydrocarbon produced 6-nitrochrysene as the only product under these conditions. Because of the symmetry present in chrysene, the expected product was 6, 12-dinitro chrysene. Interestingly, the conventional nitric acid/sulfuric acid-mediated reaction of 9, 10-dihydrophenanthrene produced a single 3-nitro-9, 10-dihydrophenanthrene as the only product. This suggests that nitration of 9, 10-dihydrophenanthrene under microwave-induced condition is very special. This may be due to the rapid exposure of the reaction with microwave. However, this is not confirmed since chrysene produced a single 6-nitrochrysene when microwave irradiation was used.

Conclusion:

In conclusion, we have developed a simple method for the nitration of 9,10-dihydrophenanthrene using a combination of kitchen microwave oven and clay-impregnated bismuth nitrate. Considering the simplicity and rapid method of nitration using non-toxic bismuth nitrate and the importance of the product, this method will find applications to cancer research.

Experimental Section:

General Procedure. General Procedures. All reactions described in this paper were carried out under a well ventilated hood. IR spectra were recorded on a Perkin-Elmer Spectrum 2000 instrument. NMR spectra were recorded on Bruker 500 MHz spectrometer. Chemical shifts were reported as δ values in parts per million downfield from tetramethyl silane as the internal standard in CDCl₃. Melting points were taken in open capillary tube and are not corrected. Column chromatography was carried out with Aldrich silica gel (230 mesh). TLC was run with precoated silica gel plate.

The compound to be nitrated (1 mmol) and Montmorillonite KSF (500 mg, Aldrich) were added to a suspension of bismuth nitrate (1 mmol) in THF (10 mL). The solvent was then evaporated under reduced pressure and dried in the vacuum pump for 5 min (in some cases the mixture needed microwave irradiation for 2 min to complete the reaction). The mixture was then repeatedly washed with dichloromethane (ca 25 mL) and it was concentrated to afford the crude product. The pure product was isolated after column chromatography and by crystallization.

Compounds 2 are known and these gave identical physico-chemical data with respect to authentic compounds.

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References:

1. (a) Banik, B. K.; Venkatraman, M. S.; Mukhopadhyay, C.; Becker, F. F. *Tetrahedron Lett.* **1998**, *39*, 7243. (b) Banik, B. K.; Ghatak, A.; Venkatraman, M. S.; Becker, F. F. *Synth. Commun.* **2000**, *30*, 2701. (c) Banik, B. K. Ghatak, A.; Mukhopadhyay, C.; Becker, F. F. *J. Chem. Res. (S)*, **2000**, 108.

2. Samajdar, S.; Becker, F. F.; Banik, B. K. *Tetrahedron Lett.* **2000**, *41*, 8017. 5. (a) Becker, F. F.; Banik, B. K. *Bioorganic & Med. Chem.* **1998**, *50*, 2877. (b) Becker, F. F.; Mukhopadhyay, C.; Hackfeld, L.; Banik, I.; Banik, B. K. *Bioorg. & Med. Chem.* **2000**, *8*, 2693. (c) Banik, B. K.; Becker, F. F. *Bioorganic & Med. Chem.* **2001**, *9*, 593.
3. For nitration with claycop, see: Gigantee, B.; Prazeres, A. O.; Marcelo-Curto, M. J.; Cornelis, A.; Laszlo, P. *J. Org. Chem.* **1995**, *60*, 3445 and references cited therein.
4. For some examples of aromatic nitration with mixed acids see: (a) Olah, G. A.; Malhotra, R.; Narang, S. C. In *Nitration. Methods and Mechanisms*, VCH Publishers: New York, **1989**. (b) Schofield, K. In *Aromatic Nitration*, Cambridge University Press: Cambridge, 1980.
5. (a) Banik, B. K., Mukhopadhyay, C., Venkatraman, M. S.; Becker, F. F. A Facile Reduction of Aromatic Nitro Compounds to Aromatic Amines by Samarium and Iodine, *Tetrahedron Lett.*, **1998**, *39*, 7343. (b) Basu, M. K., Becker, F. F.; Banik, B. K., Ultrasound-Promoted Highly Efficient Reduction of Aromatic Nitro Compounds to the Aromatic Amines by Samarium/Ammonium Chloride, *Tetrahedron Lett.*, **2000**, *41*, 6551. (c) Banik, B. K., Suhendra, M., Banik, I.; Becker, F. F. Indium/Ammonium Chloride Mediated Selective Reduction of Aromatic Nitro Compounds: Practical Synthesis of 6-Aminochrysene, *Synth. Commun.*, **2000**, *30*, 3745, (d) Banik, B. K.; Banik, I.; Becker, F. F. Indium/Ammonium Chloride-Induced Selective Reduction of Aromatic Nitro Compounds, *Organic Synthesis*, **2004**, *81*, 188.
6. (a) Banik, I.; Becker, F. F.; Banik, B. K., "Stereo selective Synthesis of β -Lactams with Polyaromatic Imines: Entry to New and Novel Anticancer Agents", *J. Med. Chem.*, **2003**, *46*, 12. (b) Banik, B. K.; Banik, I.; Becker, F. F., "Stereocontrolled Synthesis of Anticancer β -Lactams via the Staudinger Reaction", *Bioorg. Med. Chem.*, **2005**, *13*, 3611. (c) Banik, B. K.; Banik, I.; Becker, F. F., "Novel Anticancer β -Lactams", *Topics in Heterocyclic Chemistry*, **2010**, *22*, 349-373. (d) Banik, B. K.; Banik, I.; Becker, F. F., "Asymmetric Synthesis of Anticancer β -Lactams via Staudinger Reaction: Utilization of Chiral Ketene from Carbohydrate", *Eur. J. Med. Chem.*, **2010**, *45*, 846. (g) Banik, B. K.; Samajdar, S.; Becker, F. F., "Asymmetric Synthesis of Anticancer β -Lactams via Staudinger Reaction", *Mol. Med. Rep.*; **2010**, *3*, 319.

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