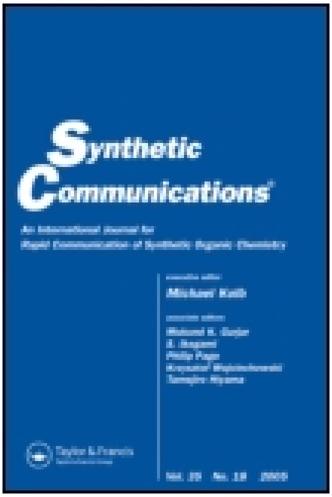

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Nitration of Aromatic Compounds by $Zn(NO_3)_2 \cdot 2N_2O_4$ and Its Charcoal-Supported System

Nasser Iranpoor [a], Habib Firouzabadi [a], Reza Heydari [a] & Morteza Shiri [a]

[a] Department of Chemistry, College of Sciences, Shiraz University, Shiraz, 71454, Iran

To cite this article: Nasser Iranpoor, Habib Firouzabadi, Reza Heydari & Morteza Shiri (2005) Nitration of Aromatic Compounds by $Zn(NO_3)_2 \cdot 2N_2O_4$ and Its Charcoal-Supported System, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 35:2, 263-270, DOI: 10.1081/SCC-200048450

To link to this article: http://dx.doi.org/10.1081/SCC-200048450

Synthetic Communications®, 35: 263–270, 2005
Copyright © Taylor & Francis, Inc.
ISSN 0039-7911 print/1532-2432 online
DOI: 10.1081/SCC-200048450

Nitration of Aromatic Compounds by $Zn(NO_3)_2 \cdot 2N_2O_4$ and Its Charcoal-Supported System

Nasser Iranpoor, Habib Firouzabadi,
Reza Heydari, and Morteza Shiri
Department of Chemistry, College of Sciences, Shiraz University,
Shiraz, Iran

Abstract: $Zn(NO_3)_2 \cdot N_2O_4$ and its charcoal supported system were found to be efficient nitrating agents. Mononitration of aromatic compounds such as benzene, alkyl benzenes, halobenzenes, nitrobenzene, anisol, and the highly selective mono-, di-, and trinitration of phenol, and dinitraion of substituted phenols were also performed in the presence of these reagents.

Keywords: Zinc nitrate, charcoal, dinitrogen tetroxide, nitration, aromatic compounds

INTRODUCTION

Aromatic nitration is among the organic reactions, which have been extensively studied. This reaction can be carried out by verities of nitrating agents such as HNO_3/H_2SO_4,[1,2] $NaNO_2/HNO_3$,[3,4] *N*-nitropyrazole/$BF_3.Et_2O/CH_2Cl_2$,[5] metallic nitrates,[6–8] $NaNO_3/H_2SO_4/NaNO_2$,[9–11] $NaNO_3/HCl/La(NO_3)_3/Et_2O \cdot H_2O$,[12] $AgNO_3/BF_3/CH_3CN$,[13] tetranitromethane,[14] clay-supported nitrates,[15,16] $AcONO_2$,[17] $BzONO_2$,[18,19] $TfONO_2$,[20] HNO_3/SiO_2,[21] pyridine derivatives carrying transferable nitro groups,[22] and montmorillonite impregnated with bismuth nitrate.[23]

Received in the UK March 8, 2004

Address correspondence to Nasser Iranpoor and Habib Firouzabadi, Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran. E-mail: iranpoor@chem.susc.ac.ir or firouzabadi@chem.susc.ac.ir

Dinitrogen tetroxide is also considered as a highly reactive nitrating agent, which its reactions are usually carried out at low temperatures and does not show selectivity for mono- or dinitartions (e.g., nitration of alkyl substituted phenols produces mono- and dinitrated isomers together with considerable amounts of nitrocyclohexadienones).[24] Very recently, NO_2/O_2 in the presence of Zeolite has been used for the nitration of moderately deactivated arenes.[25] In organic solvents such as ethyl acetate, N_2O_4 can react with metals in atomic, oxide, or salt forms to give metal nitrate complexes.[26,27] Recently, we have reported on the nitration and oxidation abilities of some of these adducts, such as $Cu(NO_3)_2 \cdot N_2O_4$, $Fe(NO_3)_3 \cdot 2N_2O_4$, and $Cr(NO_3)_3 \cdot 2N_2O_4$.[28–31] These complexes are capable to nitrate only phenolic compounds and even activated aromatic rings such as anisole cannot be nitrated by these metal nitrate/N_2O_4 complexes. In this article, we report on the use of $Zn(NO_3)_2 \cdot 2N_2O_4$ as a homogeneous reagent and its charcoal-supported system as a heterogeneous nitrating gent for the selective mono-, di-, and trinitration of phenol, dinitration of substituted phenols, and mononitration of benzene and arenes substituted with activated and moderately deactivated groups.

RESULTS AND DISCUSSION

$Zn(NO_3)_2 \cdot 2\,N_2O_4$ was prepared by complexation of zinc nitrate with dinitrogen tetroxide[23] in ethyl acetate. This compound, similar to other reported metal nitrate N_2O_4 complexes, is a delicant solid and soluble in organic solvents. When it was supported on charcoal, we obtained a heterogeneous reagent, which is easy to handle. The reactions of both $Zn(NO_3)_2 \cdot 2N_2O_4$ and its charcoal-supported system with phenol were found to be very selective and dependent on the molar ratio of nitrating agent/phenol and also the reaction temperature. The reaction with 0.75 molar equivalents of either reagent in ethyl acetate at room temperature produced a mixture of 2- and 4-nitrophenols in high yields. The reaction with $Zn(NO_3)_2 \cdot 2N_2O_4$ completes immediately, but the reaction with $Zn(NO_3)_2 \cdot 2N_2O_4$/charcoal requires 1 hr. Treatment of phenol with two molar equivalents of either of these reagents produced 2,4-dinitrophenol in 83–85% yield. When the reaction of phenol was performed with three equimolar amounts of $Zn(NO_3)_2 \cdot 2N_2O_4$ in refluxing ethyl acetate, the corresponding trinitrophenol was produced in 86% yield (Table 1). Similar to the reactions of phenol with N_2O_4 or N_2O_4-metal nitrate complexes,[28–31] the formation of some minor amounts of 1,4-benzoquinone (5–8%) in the reaction of phenol with $Zn(NO_3)_2 \cdot 2N_2O_4$ or $Zn(NO_3)_2 \cdot 2N_2O_4$/charcoal was also observed. The results of Table 1 show that the yields of the products with both reagents are very similar, but the reaction times for $Zn(NO_3)_2 \cdot 2N_2O_4$/charcoal are higher. However, handling of the reagent and workup of the reactions

Table 1. Nitration of phenol with $Zn(NO_3)_2 \cdot 2N_2O_4$ and $Zn(NO_3)_2 \cdot 2N_2O_4$/charcoal in EtOAc at room temperature

Time[a]	Molar equiv. of the reagent[a]	Yield (%)[a]	Distribution of the products (isolated yield %)[a,b]			
			2-nitro	4-nitro	2,4-dinitro	2,4,6-trinitro
1 hr (5 min)	1	90 (95)	34 (38)	56 (49)	—	—
4 hr (15 min)	2	85 (79)	—	—	85 (79)	—
12 hr[c] (15 min)[c]	3	Trace (86)	—	—	—	Trace (86)

[a] Data in the parentheses refer to the use of $Zn(NO_3)_2 \cdot 2N_2O_4$ and those out of the parentheses refer to the reaction with $Zn(NO_3)_2 \cdot 2N_2O_4$/charcoal.

[b] In all of the reactions, 5–8% of benzoquinone is also isolated.

[c] Immediately.

using $Zn(NO_3)_2 \cdot 2N_2O_4$/charcoal is much simpler than those for $Zn(NO_3)_2 \cdot 2N_2O_4$. We then used both reagents for mononitration of different substituted phenolic compounds. The results obtained for this study are shown in Table 2. Using the molar ratio of the reagent/phenolic compound (2 : 1), the selective dinitration of phenols was obtained (Table 3). This study showed that phenol can be nitrated to 2,4,6-trinitrophenol with $Zn(NO_3)_2 \cdot 2N_2O_4$, but the reaction with $Zn(NO_3)_2 \cdot 2N_2O_4$/charcoal does not occur (Table 1).

In comparison with the reactions of metal nitrate N_2O_4 complexes, which were found to nitrate only phenolic compounds,[28–31] these two reagents showed to be effective nitrating agents for phenols as well as benzene, naphthalene, and benzenes carrying activating and moderately deactivating groups. The results are shown in Table 4.

In conclusion, $Zn(NO_3)_2 \cdot 2N_2O_4$ and its charcoal-supported system are cheap and easily prepared reagents for nitration reactions. These reagents are selective for nitration of the phenolic compounds and can also be applied for the nitration of aromatic rings having activating and moderately deactivating groups.

Table 2. Mononitration of substituted phenols with one molar equivalent of $Zn(NO_3)_2 \cdot 2\ N_2O_4$/charcoal and $Zn(NO_3)_2 \cdot 2\ N_2O_4$ in CH_2Cl_2 at room temperature

Entry	Substrate	Time[a]	Product (% yield)[a,b]
1	4-Fluorophenol	(5 min) 2 hr	4-Fluoro-2-nitrophenol (98) 97
2	4-Bromophenol	(5 min) 2.5 hr	4-Bromo-2-nitrophenol (95) 95
3	4-Chlorophenol	(5 min) 2.5 hr	4-Chloro-2-nitrophenol (98) 96
4	4-Methylphenol	(5 min) 1.5 h	4-Methyl-2-nitrophenol (86) 81
5	4-Nitrophenol	(15 min) 5 hr	2,4-Dinitrophenol (93) 95
6	2-Nitrophenol	(20 min) 4 hr[c]	2,4-Dinitrophenol (78) 82
7	2,6-Dichlorophenol	(5 min) 4.25 hr	2,6-Dichloro-4-nitrophenol (98) 96
8	2,6-Dimethylphenol	(5 min) 2 hr	2,6-Dimethyl-4-nitrophenol (75)83
9	Salicylic acid	(5 min) 4 hr	2-Hydroxy-5-nitro benzoic acid (80)73 2-Hydroxy-3-nitro benzoic acid (15)20
10	Vanillin	(5 min) 0.5 hr	4-Hydroxy-3-methoxy-5-nitro benzaldehyde (80)75

[a] Data in the parentheses refer to the use of $Zn(NO_3)_2 \cdot 2\ N_2O_4$ and those out of the parentheses refer to the reactions with $Zn(NO_3)_2 \cdot 2N_2O_4$/charcoal.

[b] Isolated yield.

[c] Reflux condition.

Table 3. Dinitration of substituted phenols with two molar equivalents of either reagent[a] in CH_2Cl_2 at room temperature

Entry	Substrate	Time	Product (% yield)[b]
1	4-Fluorophenol	(5 min) 2 hr	4-Fluoro-2,6-dinitro (91) 97
2	4-Bromophenol	(10 min) 4 hr	4-Bromo-2,6-dinitro (81) 86[c]
3	4-Chlorophenol	(10 min) 3 hr	4-Chloro-2,6-dinitro (93) 87[c]
4	4-Methylphenol	(10 min) 1.25 hr	4-Methyl-2,6-dinitro (85) 80
5	4-Nitrophenol	(35 min) 12 hr	2,4,6-Trinitro (90) trace[c]
6	2-Nitrophenol	(90 min) 12 hr	2,4,6-Trinitro (86) trace[c]
7	Salicylic acid	(20 min) 10 hr	2-Hydroxy-3,5-dinitro benzoic acid (88) 60[c]
8	2-Methoxyphenol	(10 min) 1 hr	2-Methoxy-4,6-dinitro (85) 80

[a] Data in the parentheses refer to the use of $Zn(NO_3)_2 \cdot 2N_2O_4$ and those out of the parentheses refer to the reactions with $Zn(NO_3)_2 \cdot 2N_2O_4$/charcoal.

[b] Isolated yield.

[c] Under reflux condition.

EXPERIMENTAL

Thin-layer chromatography on commercial plates of silica gel 60 F_{254} was used to monitor the progress of the reactions. Column chromatography was carried out by using silica gel 60. Yields refer to isolated pure products after column chromatography. Products were characterized by comparison of their physical and spectral data with those of authentic samples. Infrared spectra were recorded on a Perkin Elmer 781 spectrometer. The NMR spectra were recorded on a Bruker Avance DPX 250. Mass spectra were recorded on a Shimadzu GCMS-QP 1000EX.

Preparation of $Zn(NO_3)_2 \cdot 2N_2O_4$

A solution of $ZnCl_2$ (34 g, 0.25 mol) in EtOAc (150 mL) was cooled to −10°C in an ice-salt bath while being stirred. Generated N_2O_4 gas[28–32] was bubbled through this solution for about 1 hr. The solvent was evaporated under reduced pressure to give $Zn(NO_3)_2 \cdot 2N_2O_4$ complex[27] as a pale yellowish deliquescent compound (79 g, 85%).

Preparation of $Zn(NO_3)_2 \cdot 2N_2O_4$ Complex/Charcoal

To a vigorously stirring solution of $Zn(NO_3)_2 \cdot 2N_2O_4$ (10 g) in dry CH_2Cl_2 (25 mL) at 0°C was added active charcoal (5 g). After 2 hr, the solvent was evaporated, and the residue was dried under vacuum. $Zn(NO_3)_2 \cdot 2N_2O_4$/charcoal powder (15 g) was obtained.

Table 4. Mononitration of aromatic compounds[a]

Arene	Conditions/Temp.	Time	Yield (%)	Distribution of product(s) (%)
Ph-H	A^b/50°C	(15 min) 6 hr	(84) 62	Ph-NO_2
Ph-Cl	A^b/rt	(30 min) 5 hr	(81) 84^d	2-Nitro(47)49, 4-Nitro(53) 51
Ph-Br	A^b/rt	(20 min) 5.5 hr	(89) 85^d	2-Nitro(39)45, 4-Nitro(61) 55
Ph-Me	A^b/rt	(15 min) 4 hr	(90) 91^d	2-Nitro(45)44, 4-Nitro(55)56
Ph-OMe	A^b/rt	(5 min) 2.5 hr	(95) 93^e	2-Nitro(40)37, 4-Nitro(60)63
Ph-NO_2	A^b/65°C	(30 min) 24 hr	(68) 0^d	1,3-Dinitro benzene
Ph-COOEt	A^b/rt	(40 min) 24 hr	(80) 0^d	3-Nitro(81) and 2-Nitro(19)
Ph-OCOMe	B^c/rt	(5 min) 2.2 hr	(94) 90^e	2-Nitro(53)55, 4-Nitro(47)45
Naphthalene	B^c/rt	(15 min) 4.5 hr	(85) 86	1-Nitro naphthalene
1,4$(MeO)_2$Ph	B^c/rt	(10 min) 2 hr	(87) 90	2-Nitro

[a] Data in the parentheses refer to the use of $Zn(NO_3)_2 \cdot 2N_2O_4$ and those out of the parentheses refer to the reactions with $Zn(NO_3)_2 \cdot 2N_2O_4$/charcoal.

[b] A: Solvent-free condition.

[c] B: CH_2Cl_2 is used as the solvent.

[d] The reaction is performed at 60°C.

[e] Reflux condition.

Mononitration of Phenol with $Zn(NO_3)_2 \cdot 2N_2O_4$/Charcoal

A mixture of phenol (0.094 g, 1 mmol) and $Zn(NO_3)_2 \cdot 2N_2O_4$ complex/charcoal (0.44 g, 0.75 mmol) in ethyl acetate (5 mL) was stirred for 1.5 hr at room temperature. The mixture was filtrated, and the residue was washed with ethyl acetate (2 × 15 mL). H_2O (15 mL) was added to the filtrate and organic layer was separated and dried over $MgSO_4$. Ethyl acetate was evaporated under vacuum. After plate chromatography on silica gel eluted with petroleum ether:acetone (8 : 2), 4-nitrophenol (0.075 g, 56%), mp 111–113°C [Lit.[33] mp 112–114°C], 2-nitrophenol (0.047 g, 34%), mp 45–46°C, [Lit.[33] mp 45–46°C] and benzoquinone (0.008 g, 5%) mp 113–114°C [Lit.[33] mp 112.5–113.5°C] were obtained.

Dinitration of Phenol with $Zn(NO_3)_2 \cdot 2N_2O_4$/Charcoal

A mixture of phenol (0.094 g, 1 mmol) and $Zn(NO_3)_2 \cdot 2\ N_2O_4$ complex/charcoal (1.11 g, 2 mmol) in ethyl acetate (5 mL) was stirred vigorously for 4 hr at room temperature. The workup was performed similar to the above-mentioned experiment. After column chromatography on silica gel eluted with petroleum ether:acetone (3 : 1), 2,4-dinitrophenol (0.156 g, 85%) mp 111–112°C [Lit.[33] 111–113°C] was obtained.

Mononitration of 4-Chlorophenol with $Zn(NO_3)_2 \cdot 2N_2O_4$

A mixture of 4-chlorophenol (0.129 g, 1 mmol) and $Zn(NO_3)_2 \cdot 2N_2O_4$ complex (0.28 g, 0.75 mmol) in CH_2Cl_2 (4 mL) was stirred vigorously at room temperature. The reaction was competed immediately. After column chromatography on silica gel using petroleum ether/acetone (8 : 2) as eluent, 4-chloro-2-nitrophenol (0.169 g, 98%) mp 90–91°C [Lit.[33] 91°C] was obtained as yellow needle crystals.

Dinitration of 4-Chlorophenol with $Zn(NO_3)_2 \cdot 2N_2O_4$

To a solution of 4-chlorophenol (0.129 g, 1 mmol) in CH_2Cl_2 (5 mL), $Zn(NO_3)_2 \cdot 2N_2O_4$ complex (0.75 g, 2 mmol) was added. The mixture was stirred for 10 min at room temperature. The mixture was chromatographed on a column of silica gel and eluted with petroleum ether/acetone (8 : 2) to give 4-chloro-2,6-dinitrphenol (0.2 g, 93%) mp 80–81°C [Lit.[33] 81°C].

Nitration of Chlorobenzene with $Zn(NO_3)_2 \cdot 2N_2O_4$/charcoal

A mixture of chlorobenzene (0.17 g, 1.5 mmol) and $Zn(NO_3)_2 \cdot 2\ N_2O_4$ complex/charcoal (0.55 g, 1 mmol) was stirred vigorously at room temperature for 30 min. The progress of the reaction was followed by GC. After completion of the reaction, the resulting mixture was dissolved in acetone (3 mL) and was presorbed on silica gel (5 g). The resulting silica gel mixture was applied on a silica gel column and eluted with petroleum ether/acetone (7 : 3) to afford 0.135 g (84%)of 2-nitro-chlorobenzene, mp 31°C [Lit.[33] 31–33°C] and 4-nitrochlorobenzene mp 80°C [Lit.[33] 81–82°C] with ratio of 47 : 53, respectively.

REFERENCES

1. Schofield, K. *Aromatic Nitration*; Cambridge University Press, 1980.
2. Vogel's. *Textbook of Practical Organic Chemistry*, 4th Ed.; Lonman: New York, 1987.
3. Germain, A. J. *Chem. Soc. Chem. Commun.* **1990**, 1697.
4. Thompson, M. J.; Zeegers, P. J. *Tetrahedron* **1991**, *47*, 8787.
5. Santaniello, E.; Ravasi, M.; Ferraboschi, P. *J. Org. Chem.* **1983**, *48*, 739.
6. Bisarya, S. C.; Joshi, S. K.; Holkar, A. G. *Synth. Commun.* **1993**, *23*, 1125.
7. Crivello, J. V. *J. Org. Chem.* **1981**, *46*, 3056.
8. Poirier, J. M.; Vottero, C. *Tetrahedron* **1989**, *45*, 1415.
9. McCullough, T. J. *Chem. Ed.* **1990**, *67*, 801.
10. Thompson, M. J.; Zeegers, P. J. *Tetrahedron Lett.* **1988**, *29*, 2471.
11. Zeegers, P. J. *J. Chem. Ed.* **1993**, *70*, 1036.
12. Ouertani, G.; Girard, P.; Kagan, H. B. *Tetrahedron Lett.* **1982**, *23*, 4315.
13. Olah, G. A.; Narang, S. C.; Olah, J. A.; Lammertsma, K. *Proc. Natl. Acad. Sci. USA* **1982**, 4487.
14. Alazard, J. P.; Kagan, H. B.; Seeton, R. *Bull. Soc. Chem. Fr.* **1977**, 499.
15. Cornelis, A.; Laszlo, P. *Synthesis* **1985**, 909.
16. Cornelis, A.; Laszlo, P. *Synlett* **1994**, 155.
17. Knowles, J. R.; Norman, R. O.C. *J. Chem. Soc.* **1961**, 3888.
18. Kurz, M. E.; Yang, L. T.A.; Zahora, E. P.; Adams, R. C. *J. Org. Chem.* **1973**, *38*, 2271.
19. Nagy, S. M.; Yarovoy, K. A.; Shakirov, M. M.; Shubin, V. G.; Votrikova, L. A.; Ione, K. G. *J. Mol. Catal.* **1991**, *64*, 31.
20. Masci, B. *Tetrahedron* **1989**, *45*, 2719.
21. Topia, R.; Torres, G.; Valderrama, J. A. *Synth. Commun.* **1986**, *16*, 681.
22. Pervez, H.; Onyisiuka, S. O.; Rees, L.; Rooney, J. R.; Sukling, C. J. *Tetrahedron* **1988**, *44*, 4555.
23. Samajdar, S.; Becker, F. F.; Banik, B. K. *Tetrahedron Lett.* **2000**, *41*, 8017.
24. Fisher, A.; Mathivanan, N. *Tetrahedron Lett.* **1988**, *29*, 1869.
25. Peng, X.; Fukui; Mizutu, M.; Suzuki, H. *Org. Biomol. Chem.* **2003**, *1*, 2326.
26. Addison, C. C.; Lewis, J. J. *Chem. Soc.* **1951**, 2843.
27. Addison, C. C. *Chem. Rev.* **1980**, *21*, 80.
28. Iranpoor, N.; Firouzabadi, H.; Zolfigol, M. A. *Synth. Commun.* **1998a**, *28*, 367.
29. Iranpoor, N.; Firouzabadi, H.; Zolfigol, M. A. *Synth. Commun.* **1998b**, *28*, 377.
30. Iranpoor, N.; Firouzabadi, H.; Zolfigol, M. A. *Synth. Commun.* **1997**, *27*, 3301.
31. Iranpoor, N.; Firouzabadi, H.; Zolfigol, M. A. *Synth. Commun.* **1998c**, *28*, 2773.
32. Mallakpour, S. E.J. *Chem. Ed.* **1992**, *69*, 238.
33. Fluka. *Chemica-Biochemical*; 1993/94.