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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

Cellulose-Supported $Ni(NO_3)_2 \cdot 6H_2O/2, 4, 6$ -Trichloro-1, 3, 5-triazine (TCT) as a Mild, Selective, and Biodegradable System for Nitration of Phenols

Firouzeh Nemati^a, Hossein Kiani^a & Yaser Saeidi Hayeniaz^b ^a Department of Chemistry, Faculty of Science, Semnan University, Semnan, Iran

^b Faculty of Chemistry, Tarbiat Moallem University, Tehran, Iran Published online: 11 Jul 2011.

To cite this article: Firouzeh Nemati , Hossein Kiani & Yaser Saeidi Hayeniaz (2011): Cellulose-Supported Ni(NO₃)₂ \cdot 6H₂O/2,4,6-Trichloro-1,3,5-triazine (TCT) as a Mild, Selective, and Biodegradable System for Nitration of Phenols, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 41:20, 2985-2992

To link to this article: <u>http://dx.doi.org/10.1080/00397911.2010.516054</u>

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Synthetic Communications[®], 41: 2985–2992, 2011 Copyright © Taylor & Francis Group, LLC ISSN: 0039-7911 print/1532-2432 online DOI: 10.1080/00397911.2010.516054

CELLULOSE-SUPPORTED Ni(NO₃)₂·6H₂O/ 2,4,6-TRICHLORO-1,3,5-TRIAZINE (TCT) AS A MILD, SELECTIVE, AND BIODEGRADABLE SYSTEM FOR NITRATION OF PHENOLS

Firouzeh Nemati,¹ Hossein Kiani,¹ and Yaser Saeidi Hayeniaz²

¹Department of Chemistry, Faculty of Science, Semnan University, Semnan, Iran

²Faculty of Chemistry, Tarbiat Moallem University, Tehran, Iran

GRAPHICAL ABSTRACT



R=H,CH₃, OH, Cl, CHO or Naphthyl

Abstract Nitration of certain phenols and naphthols in the presence of biodegradable cellulose-supported $Ni(NO_3)_2 \cdot 6H_2O/2,4,6$ -trichloro-1,3,5-triazine was carried out in acetonitrile at room temperature. Ortho nitrated phenols were obtained regioselectively within a short reaction time with good yields. The reaction condition was mild, and the employed cellulose could be recovered several times for further use.

Keywords Biodegradable; cellulose; nitration; phenols; 2,4,6-trichloro-1,3,5-triazine

INTRODUCTION

Nitration of aromatic compounds is an industrially important reaction because nitro-aromatic compounds are considered to be key building blocks for a broad range of drugs and pharmaceuticals.^[1] Among these compounds, *o*-nitro phenols and naphthols are widely used for the synthesis of commercially valuable compounds such as dyes, pharmaceuticals, plastics, and explosives.^[2]

In the classic procedure for the nitration of phenols, use of nitric and sulfuric acid mixtures would result in the formation of *ortho* and *para* products with a ratio of about 2:1.^[3] Because of these disadvantages, it is desirable to develop a new method showing more regioselectivity and using less toxic reagents.

Many new versions of this classic procedure are reported in literature, mostly using new nitration agents or acid catalysts such as impregnated alumina and silica

Received April 14, 2010.

Address correspondence to Firouzeh Nemati, Department of Chemistry, Faculty of Science, Semnan University, Semnan, Iran. E-mail: fnemati_1350@yahoo.com

with N₂O₄,^[4] claycop,^[5] montmorillonite impregnated with bismuth nitrate,^[6] clayfen,^[7] zeofen,^[8] modified silica,^[9] metal nitrates,^[10] nitronium tetrafluoro borate,^[11] zirconyl nitrate,^[12] ionic liquids,^[13] zeolite-based solid acid catalysts,^[14] peroxy nitrile,^[15] Yb(OTf)₃ and Hf(OTf)₄ in conjunction with HNO₃,^[16] nitrogen oxides,^[17] heteropoly acids,^[18] MCM-41,^[19] Zn(NO₃)₂ · 2 N₂O₄ and its charcoal-supported system,^[20] polyethylene glycol (PEG)–N₂O₄,^[21] *tert*-butyl nitrite in solution and on solid support,^[22] aluminum nitrate and silica sulfuric acid,^[23] metal salts impregnated with Yb-Mo-montmorillonite KSF,^[24] and nano-sized tungsten oxide supported on sulfated SnO₂.^[25]

The new trends in science and technology toward using natural materials and reusable systems, in addition to the environmental hazards of the current methods, make green and ecofriendly methods for regioselective nitration of phenols desirable. Some of the newly investigated alternatives that could fit these standards are natural biopolymers, especially cellulose, which could be used as a support for sulfuric acid.^[26,27]

RESULTS AND DISCUSSION

In continuation of our earlier studies of organic transformations,^[28–31] here we report our results on the regioselective nitration of some phenols using cellulose-supported Ni(NO₃)₂ · $6H_2O$, with excellent yields in the presence of 3 mol% of 2,4,6-trichloro-1,3,5-triazine (TCT) at room temperature in acetonitrile TCT (cyanuric chloride) (Scheme 1) was employed as a cheap and commercially available reagent.^[32] It performed as the required acid catalyst source in the nitration process instead of Brønsted or Lewis acids. Actually, TCT reacts with incipient moisture and releases 3 mol of HCl and cyanuric acid, which is the by-product of this reaction^[33] (Scheme 1).

Using cellulose-supported Ni(NO₃)₂ \cdot 6H₂O for the nitration of phenols is a brand new idea that has several advantages. One of the most important advantages is the noncorrosiveness of TCT, which is a crucial factor for industrial applications. The by-product, cyanuric acid, can be easily removed by washing the reaction mixture with water.

Nitration of phenol was examined in the presence of TCT and various metal nitrates and conditions. Initially, the reaction of phenol with some metal nitrates was selected as a model. We used acetonitrile solution of phenol (1 mmol) and metal



Scheme 1. Reaction of TCT with water, producing NO_2^+ .

Entry	Metal nitrates	TCT (mmol)	Time (h)	o-Nitro phenol (%)	
1	NaNO ₂	0.03	18	60	
2	NaNO ₃	0.03	16	55	
3	$Cr(NO_3)_3 \cdot 9H_2O$	0.03	1	40	
4	$Fe(NO_3)_3 \cdot 9H_2O$	0.02	0.5	55	
5	$Fe(NO_3)_3 \cdot 9H_2O$	0.03	0.5	55	
6	$Co(NO_3)_2 \cdot 6H_2O$	0.03	10	50	
7	$Ni(NO_3)_2 \cdot 6H_2O$	0.02	4	60	
8	$Ni(NO_3)_2 \cdot 6H_2O$	0.03	2	75	
9	$Mn(NO_3)_2 \cdot 4H_2O$	0.02	5	55	
10	$Mn(NO_3)_2 \cdot 4H_2O$	0.03	3	75	
11	$Bi(NO_3)_3 \cdot 5H_2O$	0.03	9	60	
12	$Zn(NO_3)_2 \cdot 6H_2O$	0.03	1.5	80	
13	$Cu(NO_3)_2 \cdot 3H_2O$	0.03	7	60	

Table 1. Nitration of phenol using different metal nitrates in the presence of 2 or 3 mol% TCT in acetonitrile at room temperature

nitrates (1 mmol) in the presence of different amounts of TCT, which was stirred at room temperature for 0.5–18 h. The results are summarized in Table 1.

Some good results were observed in the presence of Ni(NO₃)₂ · $6H_2O$, Mn(NO₃)₂ · $4H_2O$, and Zn(NO₃)₂ · $6H_2O$ (Table 1, entries 8, 10, and 12), but generally the reaction time was long.^[34] Surprisingly, a remarkable regioselectively and short reaction time was observed when those metal nitrates were supported on cellulose in 3% mol of TCT and treated with phenol in acetonitrile. Within the results, the *ortho*-isomer was an exclusive product (Table 2, entries 2, 4, and 6). Apparently, cellulose-supported Ni(NO₃)₂ · $6H_2O$ shows the most *ortho*-selectivity with the shortest reaction time (Table 2, entry 6). An increase in the amount of TCT or cellulose-supported reagent has no obvious effect on the results of the reaction.

According to the obtained data, use of 0.5 g cellulose-supported Ni(NO₃)₂ · 6H₂O in presence of 3% mol TCT in acetonitrile is the best circumstance for the nitration of phenol.

Entry	Reagent	Reagent (g)	TCT (mmol)	Time (min)	<i>o</i> -Nitro phenol (%)
1	Cellulose–Zn(NO ₃) ₂ · 6H ₂ O	0.5	0.02	90	60
2	Cellulose– $Zn(NO_3)_2 \cdot 6H_2O$	0.5	0.03	60	80
3	Cellulose–Mn(NO ₃) ₂ · $4H_2O$	0.5	0.02	90	55
4	Cellulose– $Mn(NO_3)_2 \cdot 4H_2O$	0.5	0.03	60	75
5	Cellulose-Ni(NO ₃) ₂ ·6H ₂ O	0.5	0.02	60	75
6	Cellulose-Ni(NO ₃) ₂ · 6H ₂ O	0.5	0.03	45	80
7	Cellulose-Ni(NO ₃) ₂ · 6H ₂ O	0.5	0.04	45	80
8	Cellulose-Ni(NO ₃) ₂ · 6H ₂ O	0.6	0.03	45	80
9	Cellulose-Ni(NO ₃) ₂ · 6H ₂ O	0.7	0.03	45	70
10	Physical mixture of cellulose and $Ni(NO_3)_2 \cdot 6H_2O$	0.5 g cellulose and 1 mmol $Ni(NO_3)_2 \cdot 6H_2O$	0.03	90	75

 Table 2. Nitration of phenol using cellulose-supported metal nitrates in the presence of TCT in acetonitrile at room temperature

Entry	Substrate	Products	Time (min)	Yield (%) ^a
1	Phenol	o-Nitro phenol	45	80
2	Naphthalen-1-ol	2-Nitronaphthalen-1-ol	45	80
3	Naphthalen-2-ol	1-Nitronaphthalen-2-ol	50	90
4	<i>m</i> -Cresol	5-Methyl-2-nitrophenol	30	65
5	Resorcinol	4-Nitrobenzene-1,3-diol	30	60
6	2-Hydroxybenzaldehyde	2-Hydroxy-3-nitrobenzaldehyde	50	80
7	2-Chlorophenol	2-Chloro-6-nitrophenol	60	85
8	4-Chlorophenol	4-Chloro-2-nitrophenol	40	90
9	p-Cresol	4-Methyl-2-nitrophenol	30	90

Table 3. Nitration of phenols using 0.5 g cellulose-supported $Ni(NO_3)_2 \cdot 6H_2O$ in the presence of 0.03 mmol TCT in acetonitrile at room temperature

^aYields are based on isolated products.

The extent of generality of this reaction is shown with several examples in Table 3. All the selected phenols yielded exclusively the *o*-nitro product in good to excellent yields.

Thus, cellulose provides an ideal system for milder, safer, and more regioselective nitration of phenols. It is also reusable and ecofriendly.



Scheme 2. Plausible mechanism.

Table 4. Comparison of results using cellulose-supported $Ni(NO_3)_2 \cdot 6H_2O/TCT$ with results obtained by other workers for the nitration of phenol

Entry	Nitrating agent and acid catalyst	Conditions	Time (min)	Yield ^a (%)	Ref.
1	MCM-41/HNO3 30%	DCE/rT	120	90	19
2	WSSnO ₂ ^b /HNO ₃	60 °C	60	80	25
3	$ZrO(NO_3)_2 \cdot xH_2O$	Acetone/rT	30	40	12
4	Metal-modified KSF/HNO ₃	THF/30°C	720	41	40
5	Mg(HSO ₄) ₂ /NaNO ₃ /wet SiO ₂	CH_2Cl_2/rT	30	36	37
6	NaNO ₂ /SSA/wet SiO ₂	CH_2Cl_2/rT	90	30	36
7	Acetyl nitrate/SiO ₂	CHCl ₃ /-20°C	120	93	35
8	Cellulose-supported Ni(NO ₃) ₂ · 6H ₂ O/TCT	CH ₃ CN/rT	45	80	

^ao-Nitro phenol.

^bNano-sized tungsten oxide supported on sulfated SnO₂.

The suggested mechanism is depicted in Scheme 2. We propose that cellulose acts as a template by forming hydrogen bonds between their OH groups, phenol, and nitrate anions. This complex would transform into the intermediate and then undergoes a rearrangement to o-nitro phenol.^[35]

In Table 4, the efficiency of our method for the nitration of phenols is compared with some other published works in literature. Each of these methods has its own advantages, but they all suffer from some disadvantages, including difficulty in preparation of reagent or catalyst (entry 2), poor regioselectivity (entries 3, 4, 5, and 6), use of corrosive reagent (entries 1, 2, and 4), long reaction time (entry 4), and harsh reaction condition (entry 7).

EXPERIMENTAL

Chemicals were purchased from the Fluka, Merck, and Aldrich chemical companies. Melting points were determined on an Electrothermal 9100, without further corrections. The nitration products are characterized through comparison of their spectral data [infrared (IR), ¹H NMR], thin-layer chromatography (TLC), and melting points with the corresponding authentic samples reported in literature.

General Procedure for Preparation of Cellulose-Supported Metal Nitrates

The reagents were prepared by impregnation: Metal nitrates (2.5 g) were dissolved in the mixture of H₂O and acetone (20.0 ml, 50:50). After addition of cellulose (5.0 g), the solution was stirred for 1 h using a magnetic stirrer at room temperature $(20 \,^{\circ}\text{C})$. The excess solvent was removed by a vacuum rotary under mild vacuum pressure, and finally the remaining solid was dried in a vacuum oven at room temperature for 6 h.

Recycling of Cellulose

Cellulose was separated from the reaction mixture by paper filtration. Then it was washed thoroughly with H_2O and acetone and dried in a vacuum oven for 8 h to give recycled cellulose. It can be reused in the preparation of reagent up to three times.

Typical Procedure for Mononitration of Phenols

Phenol (0.094 g, 1 mmol), cellulose-supported metal nitrates (0.5 g), and TCT (0.006 g, 0.03 mmol) were stirred in 5 mL of acetonitrile at room temperature. After the completion of the reaction, the reaction mixture was filtered (the progress of the reaction was monitored by TLC). The residue was washed with acetonitrile (2–5 mL) and dried over anhydrous sodium sulfate, and finally the solvent was removed under vacuum (35–40 °C). The crude product was treated with *n*-pentane (4-nitrophenol is insoluble in *n*-pentane), and then the *n*-pentane was evaporated by water bath (35–40 °C) to give 2-nitrophenol. The yield was 0.11 g (80%), mp 43 °C (lit.^[36] mp 44 °C).

The other nitro phenols were purified by silica-gel dry flash chromatography using petroleum ether–ethyl acetate (98:2) as eluent.

Spectral (IR, ¹H NMR) and Analytical Data

5-Methyl-2-nitrophenol (Entry 4, Table 3). Mp 53–54 °C (lit.^[10] mp 53–56 °C); IR (KBr) v_{max} (cm⁻¹): 3249, 1632, 1332, 766; ¹H NMR (300 MHz; CDCl₃; Me₄Si): δ 10.75 (s, 1H), 7.79 (d, J = 8.4 Hz, 1H), 6.91 (s, 1H), 6.76 (d,d, J = 8.4, J = 0.9 Hz, 1H), 2.29 (s, 3H).

4-Methyl-2-nitrophenol (Entry 9, Table 3). Mp 32–33°C (lit.^[37] mp 31 °C); IR (KBr) υ_{max} (cm⁻¹): 3254, 1634, 1539, 1323; ¹H NMR (300 MHz; DMSO; Me₄Si): δ 10.63 (s, 1H), 7.67 (s, 1H), 7.35–7.32 (m, 1H), 7.01 (d, J = 8.46 Hz, 1H), 2.24 (s, 3H).

2-Hydroxy-3-nitrobenzaldehyde (Entry 6, Table 3). Mp 107–108 °C (lit.^[38] mp 105–109 °C);¹H NMR (300 MHz; CDCl₃; Me₄Si): δ 11.84 (s, br, 1H), 10.27 (s, 1H), 8.34 (d, d, J=9.1, J=2.9 Hz, 1H), 8.25 (d, d, J=8.1, J=1.7 Hz, 1H), 8.04 (d, J=7.6, J=1.7 Hz, 1H).

1-Nitronaphthalen-2-ol (Entry 3, Table 3). Mp: $100-102 \,^{\circ}\text{C}$ (lit.^[39] mp $104 \,^{\circ}\text{C}$); ¹H NMR (300 MHz; CDCl₃; Me₄Si): δ 11.39 (s, 1H), 8.02 (d, J=9 Hz, 1H), 7.94 (d, J=8.1 Hz, 1H), 7.64–7.54 (m, 3H), 7.32 (d, J=9 Hz, 1H).

CONCLUSION

In summary, the *ortho* nitration of phenols in the presence of cellulose-supported Ni(NO₃)₂ \cdot 6H₂O and a catalytic amount of TCT has been achieved with high regioselectivity and excellent yields. This procedure has several advantages in comparison to the other reported methods including use of inexpensive acid catalyst and biodegradable and reusable reagents along with easily accessible nitration agent. The temperature-control-free nature of this process made it a green methodology with wide synthetic and commercial utility. It is also worth mentioning that the by-product of the preparation of TCT is cyanuric acid, which can be easily removed by washing.

ACKNOWLEDGMENT

We thank the Department of Chemistry and Office of Gifted Students at Semnan University for financial support.

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