This article was downloaded by: [Stony Brook University] On: 23 October 2014, At: 14:50 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Transfer Hydrogenation of Aromatic Nitro Compounds Using Polymer-Supported Formate and Pd-C

K. Abiraj^a, G. R. Srinivasa^a & D. Channe Gowda^a ^a Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore, Karnataka, 570 006, India Published online: 28 Jul 2007.

To cite this article: K. Abiraj, G. R. Srinivasa & D. Channe Gowda (2005) Transfer Hydrogenation of Aromatic Nitro Compounds Using Polymer-Supported Formate and Pd-C, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 35:2, 223-230, DOI: <u>10.1081/SCC-200048429</u>

To link to this article: <u>http://dx.doi.org/10.1081/SCC-200048429</u>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the

Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions



Transfer Hydrogenation of Aromatic Nitro Compounds Using Polymer-Supported Formate and Pd-C

K. Abiraj, G. R. Srinivasa, and D. Channe Gowda

Department of Studies in Chemistry, University of Mysore, Mysore, Karnataka, India

Abstract: Transfer hydrogenation of aromatic nitro compounds using recyclable polymer-supported formate as hydrogen donor and Pd-C as a catalyst produces corresponding amines in excellent yields (90–98%).

Keywords: Nitro compounds, catalytic transfer hydrogenation, polymer-supported formate, 10% Pd-C, amines

INTRODUCTION

Reduction of aromatic nitro compounds to the corresponding amines is an important transformation. A number of reagents have been developed for this purpose.^[1,2] The heterogeneous catalytic transfer hydrogenation (CTH) using hydrogen donors (e.g., ammonium formate) is safer, cost-effective, highly selective, rapid, and environmental friendly.^[3–9] Various hydrogen donors such as cyclohexene,^[10,11] 1,4-cyclohexadiene,^[12,13] hydrazine,^[14,15] formic acid,^[4,9] ammonium formate,^[7,16,24] propan-2-ol,^[7,17] triethyl-ammonium formate,^[18,19] and hydrazinium monoformate,^[3,25] have been developed for CTH. Ammonium formate sublimes and therefore has limitation.

Received in India November 8, 2004

Address correspondence to D. Channe Gowda, Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore, Karnataka 570 006, India. Fax: 091-0821-2421263/2518835; E-mail: dcgowda@yahoo.com

Request Permissions / Order Reprints

powered by **RIGHTSLINK**



R = halogen, -CH=CH₂, -CN, -CHO, -COR, -CONH₂, -OCH₃ and -OH.

Scheme 1.

Desai and Danks^[20] and^[21] performed the transfer hydrogenation of alkenes using polymer-supported formate as hydrogen donor in the presence of Wilkinson's catalyst and Pd(OAc)₂. However, it has been observed that controlling the reduction rates is difficult with these active homogeneous catalysts. The use of heterogeneous catalysts offers certain advantages, and we report the 10% palladium on carbon catalyzed facile reduction of aromatic nitro compounds to the corresponding amines using polymer-supported formate as hydrogen donor at room temperature (Scheme 1).

A wide range of structurally varied nitroarenes underwent reduction, and the results are summarized in Table 1. All the amine derivatives were characterized by comparison of their TLC, melting points, IR spectra, and ¹H-NMR spectra with authentic samples. The reactions are reasonably fast and high yielding (90–98%). The selectivity observed during the reduction of nitro derivatives in the presence of sensitive functional groups such as halogen^[14,16] (entries 1–3 & 12), alkene^[6,7] (entry 4), nitrile^[3,17] (entry 5), and carbonyl^[9,17,26] (entries 6 and 7) group, was remarkable.

The separation of the amino derivatives from the reaction mixture involved filtration to remove the catalyst and resin followed by evaporation of the solvent. The crude product was of excellent purity in most of the cases. The water-soluble aromatic amines are produced in high yields (entries 1, 12-16). Ten successive recycle runs were possible with polymer-supported formate before there was an appreciable decrease in the reaction yield (Table 2).

In conclusion, we developed a novel CTH system for the clean and efficient reduction of aromatic nitro compounds to the corresponding amines using polymer-supported formate and 10% Pd-C.

EXPERIMENTAL

Materials

¹H-NMR spectra were recorded on an AMX-400 MHz spectrometer using CDCl₃ as the solvent and TMS as internal standard. The IR spectra were

17
2
сч Ц
õ
¹⁰
c
0
3
$\overline{\mathbf{C}}$
20
4
-
at
$\overline{}$
Ë
rs
ve Ve
-È
5
õ
Ĕ
щ
Ŋ
ō
$\overline{\mathbf{v}}$
_
Ę.
g
de
)ai
Ę
Ν
6
Ω

Lit 63 [22] 99 [22] 71 ^[22] mp (°C) Found 00 - 10162 - 6470-71 Yield^a 95^b $\binom{0}{2}$ 98 96 $-NH_2$ -NH2 Product Б $\dot{\overline{O}}$ Time (\mathbf{q}) 2.0 2.0 3.0 -N02 -NO₂ Substrate ቯ ក់ Entry 2 3





213-214 ^[22]

 $211 - 212^{c,d}$

93

-NH,

4.0

-NO,

-NO₂

-NH2

45-48 [22]

46 - 48

95

Ē

ŚŻ

4.5

ő - (continued)

106 ^[23]

04 - 106

94

Į

H₃COC-

5.0

όΥ-

H_scoc-

72 ^[22]

70-71

95

-NH2

-OHO

4.0

-N02

OHC-

9

g

Ś

4

p (°C)	Lit	114 [22]	88 [22]	206 [22]	112 [22]
łuı	Found	112–114	85-87	206–207	110-112
<i>b</i> 11 .77	Y 1eld ⁻ (%)	92	94 ^b	06	94 ^b
	Product	H ₂ NOC		H ² OH	CH ₃
Ė	(h)	3.5	5.0	4.5	3.0
	Substrate	H ₂ NOC	OMe NO2	e S S S S S S S S S S S S S S S S S S S	CH ₃
	Entry	8	6	10	11

Table 1. Continued

Downloaded by [Stony Brook University] at 14:50 23 October 2014

K. Abiraj, G. R. Srinivasa, and D. C. Gowda



^{*a*}Yields of isolated products.

^cBoiling point.

 d The spectra were compared with those of a commercial sample.

^bIsolated as acetyl derivative.

Cycle	1	2	3	4	5	6	7	8	9	10
Time (hr)	2.0	2.5	2.5	3.0	3.0	3.5	4.0	4.5	5.0	5.0
Yield (%)	98	96	96	94	93	92	92	92	91	90

Table 2. Recycling of polymer-supported formate for the reduction of *p*-chloronitrobenzene

recorded on Shimadzu FTIR- 8300 spectrometer. The melting points were determined by using Thomas–Hoover melting point apparatus and are uncorrected. Thin-layer chromatography was carried out on silica gel plates obtained from Whatman Inc. The substrates were either commercial products and were used as purchased or were prepared according to literature procedures. Aminomethyl polystyrene resin was purchased from Advanced Chemtech (1% DVB cross-linked, 100–200 mesh, 2 mmol/g). 10% Pd-C was purchased from E-Merck (India) Ltd. All of the solvents used were analytical grade or were purified according to standard procedures.

Preparation of Polymer-Supported Formate

The polymer-supported formate was prepared by washing aminomethyl polystyrene resin with 50% solution of formic acid in dichloromethane. The resulting polymer was washed successively with dichloromethane and ether, and dried. The resin was used as such for the reduction.

General Procedure for the Reduction of Aromatic Nitro Compounds

To a solution of nitro compound (5 mmol) in methanol (15 mL) taken in a horizontal solid phase vessel, polymer-supported formate (1.5 g) and 10% Pd-C (100 mg) were added. The suspension was shaken well¹ for the specified time at room temperature (Table 1). After consumption of the starting material, the reaction mixture was filtered and washed thoroughly with methanol. The combined washings and filtrate were evaporated. The crude product was found to be analytically pure in most cases. Wherever necessary, the crude product was taken into organic layer and washed with

¹The reaction mixture was subjected to shaking using a manual shaker as the shaking of the polymer-supported formate instead of stirring increases its life for recycling purpose.

Transfer Hydrogenation of Aromatic Nitro Compounds

saturated sodium chloride. For recycling purposes, the residue containing polymer-supported formate and the catalyst was washed thoroughly and successively with DMF, dichloromethane, 50% solution of formic acid in dichloromethane, dichloromethane, and ether. Thus, activated resin along with the catalyst was dried under vacuum and used as such for further reduction reactions.

ACKNOWLEDGMENTS

We gratefully acknowledge financial support from the University Grants Commission, New Delhi. We also acknowledge Council of Scientific and Industrial Research, New Delhi, for a research fellowship (to KA).

REFERENCES

- Kabalka, G. W.; Varma, R. S. Reduction of Nitro and Nitroso Compounds. In Comprehensive Organic Synthesis; Trost, B. M., Fleming, I. J., Eds.; Pergamon Press: Oxford, 1991; Vol. 8, pp. 363–379.
- Tafesh, A. M.; Weiguny, J. A review of the selective catalytic reduction of aromatic nitro compounds into aromatic amines, isocyanates, carbamates, and ureas using CO. *Chem Rev.* 1996, 96, 2035–2052.
- Gowda, D. C. Magnesium/hydrazinium monoformate: a new hydrogenation method for the removal of some commonly used protecting groups in peptide synthesis. *Tetrahedron Lett.* 2002, 43, 311–313.
- Gowda, D. C.; Gowda, A. S.; Baba, A. R.; Gowda, S. Nickel-catalyzed formic acid reductions: a selective method for the reduction of nitro compounds. *Synth. Commun.* 2000, *30*, 2889–2895.
- Johnstone, R. A. W.; Wibly, A. H.; Entwistle, I. D. Heterogeneous catalytic transfer hydrogenation and its relation to other methods of reduction of organic compounds. *Chem. Rev.* 1985, 85, 129–170.
- Paryzek, Z.; Koenig, H.; Tabaczka, B. Ammonium formate/palladium on carbon: a versatile system for catalytic hydrogen transfer reductions of carbon-carbon double bonds. *Synthesis* 2003, 2023–2026.
- Selvam, P.; Mohapatra, S. K.; Sonavane, S. U.; Jayaram, R. V. Chemo- and regioselective reduction of nitroarenes, carbonyls and azo dyes over nickelincorporated hexagonal mesoporous aluminophosphate molecular sieves. *Tetrahedron Lett.* 2004, 45, 2003–2007.
- Wiener, H.; Blum, J.; Sasson, Y. Studies on the mechanism of transfer hydrogenation of nitroarenes by formate salts catalyzed by Pd/C. J. Org. Chem. 1991, 56, 4481–4486.
- Yu, J.-Q.; Wu, H.-C.; Ramarao, C.; Spencer, J. B.; Ley, S. V. Transfer hydrogenation using recyclable polyurea-encapsulated palladium: efficient and chemoselective reduction of aryl ketones. *Chem. Commun.* 2003, 678–679.
- 10. Daga, M. C.; Taddei, M.; Varchi, G. Tetrahedron Lett. 2001, 42, 5191-5194.

- Khan, S. A.; Sivanandaiah, K. M. Catalytic transfer hydrogenation in solid-phase peptide synthesis: synthesis of bradykinin. *Synthesis* 1978, 750–751.
- Bajwa, J. S. Chemoselective deprotection of benzyl esters in the presence of benzyl ethers by catalytic transfer hydrogenation. *Tetrahedron Lett.* 1992, 33, 2299–2302.
- Felix, A. M.; Heimer, E. P.; Lambros, T. J.; Tzougraki, C.; Meienhofer, J. Rapid removal of protecting groups from peptides by catalytic transfer hydrogenation with 1,4-cyclohexadiene. J. Org. Chem. 1978, 43, 4194–4196.
- Cellier, P. P.; Spindler, J.-F.; Taillefer, M.; Cristau, H.-J. Pd/C-catalyzed roomtemperature hydrodehalogenation of aryl halides with hydrazine hydrochloride. *Tetrahedron Lett.* 2003, 44, 7191–7195.
- Yuste, F.; Saldana, M.; Walls, F. Selective reduction of aromatic nitro compounds containing *O*- and *N*-benzyl groups with hydrazine and raney nickel. *Tetrahedron Lett.* 1982, 23, 147–148.
- Ram, S.; Ehrenkaufer, R. E. Ammonium formate in organic synthesis: a versatile agent in catalytic transfer hydrogenation. *Synthesis* 1988, 91–97.
- Mebane, R. C.; Jensen, D. R.; Rickerd, K. R.; Gross, B. H. Transfer hydrogenation of nitriles with 2-propanol and raney nickel. *Synth. Commun.* 2003, 33, 3373–3379.
- Abiraj, K.; Srinivasa, G. R.; Gowda, D. C. Novel and efficient synthesis of symmetrical functionalized biaryls using zinc and triethylammonium formate. *Synlett* 2004, 877–879.
- Srinivasa, G. R.; Abiraj, K.; Gowda, D. C. The synthesis of azo compounds from nitro compounds using lead and triethylammonium formate. *Tetrahedron Lett.* 2003, 44, 5835–5837.
- Desai, B.; Danks, T. N. Thermal and microwave-assisted hydrogenation of electron-deficient alkenes using a polymer-supported hydrogen donor. *Tetrahedron Lett.* 2001, 42, 5963.
- Basu, B.; Bhuiyan, M. M. H.; Das, P.; Hossain, I. Catalytic transfer reduction of conjugated alkenes and an imine using polymer-supported formates. *Tetrahedron Lett.* 2003, 44, 8931.
- Vogel, A. I. *Text Book of Practical Organic Chemistry*, 5th Ed.; Furniss, B. S., Hannaford, A. J., Smith, P. W. G., Tatchell, A. R., Eds.; Addition Wesely Longman Limited: UK, 1997, p. 1298.
- Vogel, A. I. *The Merck Index*, 11th Ed.; Budavari, S., Ed.; Merck & Co., Inc.: USA, 1989.
- Gowda, S.; Abiraj, K.; Gowda, D. C. Reductive cleavage of azo compounds catalyzed by commercial zinc dust by using ammonium formate or formic acid. *Tetrahedron Lett.* 2002, 43, 1329–1331.
- Gowda, S.; Gowda, D. C. Application of hydrazinium monoformate as new hydrogen donor with raney nickel: a facile reduction of nitro and nitrile moieties. *Tetrahedron* 2002, 58, 2211–2213 references therein.
- 26. Selvam, P.; Sonavane, S. U.; Mohapatra, S. K.; Jayaram, R. V. Selective reduction of alkenes, α , β -unsaturated carbonyl compounds, nitroso compounds, N,N-hydrogenolysis of azo and hydrazo functions as well as simultaneous hydrodehalogenation and reduction of substituted aryl halides over PDMCM-41 catalyst under transfer hydrogenation conditions. *Tetrahedron Lett.* **2004**, *45*, 3071–3075.