

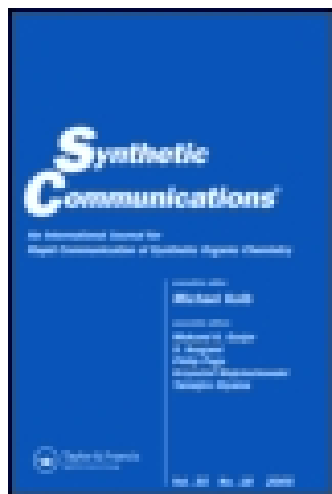
This article was downloaded by: [Temple University Libraries]

On: 08 January 2015, At: 09:10

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/lcyc20>

The Reduction of Aromatic Aldehydes to Hydrocarbons with Borohydride Exchange Resin (BER)-Nickel Acetate in Methanol

B. P. Bandgar^a, S. N. Kshirsagar^a & P. P. Wadgaonkar^b

^a Department of Chemistry, R.B.N.B. College, Shrirampur, 413709, Maharashtra State, India

^b Polymer Chemistry Division, National Chemical Laboratory, Pune, 411008, Maharashtra State, India
Published online: 23 Sep 2006.

To cite this article: B. P. Bandgar, S. N. Kshirsagar & P. P. Wadgaonkar (1995) The Reduction of Aromatic Aldehydes to Hydrocarbons with Borohydride Exchange Resin (BER)-Nickel Acetate in Methanol, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 25:7, 941-945, DOI: [10.1080/00397919508012655](https://doi.org/10.1080/00397919508012655)

To link to this article: <http://dx.doi.org/10.1080/00397919508012655>

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>

**THE REDUCTION OF AROMATIC ALDEHYDES
TO HYDROCARBONS WITH BOROHYDRIDE EXCHANGE
RESIN (BER)-NICKEL ACETATE IN METHANOL¹**

B.P. Bandgar,^{a*} S.N.Kshirsagar,^a and P.P.Wadgaonkar^b

^a Department of Chemistry, R.B.N.B. College, Shrirampur - 413709,
Maharashtra State, India

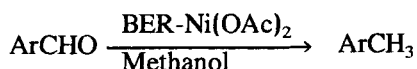
^b Polymer Chemistry Division, National Chemical Laboratory,
Pune - 411008, Maharashtra State, India

Abstract : Aromatic aldehydes were reduced to the corresponding hydrocarbons with borohydride exchange resin (BER) - nickel acetate in methanol in excellent yields.

Apart from the classical methods involving Clemmensen² and Wolf-Kishner reductions³ several reagents have been developed for the reduction of aromatic aldehydes to the corresponding hydrocarbons.⁴⁻⁷ Borohydride exchange resin (BER) an useful reducing reagent⁸ has been utilized in several organic transformations.⁹⁻¹¹ BER is much more stable in the presence of nickel boride, and BER-nickel acetate system was shown to be capable of reducing alkenes,¹² nitro compounds,¹³ azides¹⁴ and aryl halides.¹⁵

★ To whom correspondence should be addressed.

We now wish to report the conversion of ArCHO to ArCH₃ using BER-Ni(OAc)₂ in methanol (scheme). With this reducing system



simultaneous dechlorination of aryl halide (entry 4) and reduction of nitro group to the amino group (entry 5) took place. The reduction of less reactive aromatic aldehydes (entries 10,11) to the corresponding hydrocarbons did not occur even after refluxing for 9 h. The corresponding alcohols however, were isolated as the reduction products.

BER-Ni(OAc)₂ reducing system has significant advantages over other conventional methods.²⁻⁷ Simple procedure which does not require drastic acidic or alkaline conditions or high temperature. The resin could be used repeatedly on regeneration by treating it with 2N HCl. The isolation of pure products by simple filtration and evaporation is an important feature of this method.

In conclusion, BER-Ni(OAc)₂ system in methanol is a reagent of choice for the reduction of aromatic aldehydes to the corresponding hydrocarbons because of its simplicity of performance, excellent yield and milder reaction conditions.

Experimental :

All chemicals were of analytical grade. The solvents were distilled before use. Commercially available sodium borohydride was used as received. Amberlite IRA-400 (chloride form) was used as an ion exchange resin for supporting borohydride anion. All glassware was oven-dried.

The products were characterized by their physical constants and spectral characteristics (¹H NMR, IR etc.). ¹H NMR spectra were recorded in CDCl₃ on 60 MHz or FT 90 MHz instrument using TMS as internal reference. IR spectra were recorded in nujol on Perkin Elmer IR spectrometer : model PE - 883.

Preparation of Borohydride Exchange Resin.

An aqueous solution of sodium borohydride (0.5 M, 100 mL) was stirred with 10 g of wet, chloride-form resin (Amberlite IRA-400 anion exchange resin) for 1 h. The resulting resin was washed thoroughly with distilled water until free of excess sodium borohydride. The borohydride bound ion exchange resin was then dried in vacuo at 60°C for 5 h. The dried resin was analyzed for borohydride content by hydrogen evolution on acidification with 0.05 N hydrochloric acid; the average capacity of the ion exchange resin was found to be 3 mmol BH₄⁻ per gram of dry resin. The dried resin was stored under nitrogen at room temperature. The hydride content was constant over 6 weeks.

The Reduction of Aromatic Aldehydes : General procedure.

BER (15 mmol) was added to Ni(OAc)₂ (0.5 mmol) in methanol. Aromatic aldehyde (5 mmol) was added, and stirred at room temperature for 4-5 h (entries 1-5) or refluxed for 2-3 h (entries 6-11). The progress of the reaction was monitored by TLC. The resin was filtered, washed with methanol (4x10 ml) and the combined filtrate was evaporated under reduced pressure to give a residue. It was dissolved in diethyl ether and insoluble nickel salt was removed by filtration. The ether

Table 1. Reduction of Aromatic aldehydes with BER-Ni(OAc)₂ in Methanol.

entry	aldehyde	product	yield(%) ^a
1.	2-Furfuraldehyde	2-Methyl-Furan	86
2.	Ph-CHO	Ph-CH ₃	91
3.	4-CH ₃ .C ₆ H ₄ .CHO	1,4-(CH ₃) ₂ C ₆ H ₄	92
4.	4-Cl.C ₆ H ₄ .CHO	Ph-CH ₃	95
5.	3-NO ₂ -C ₆ H ₄ .CHO	3-NH ₂ -C ₆ H ₄ .CH ₃	97
6.	2-OH.C ₆ H ₄ .CHO	2-OH.C ₆ H ₄ .CH ₃	98
7.	3-H ₃ CO.C ₆ H ₄ .CHO	3-H ₃ CO.C ₆ H ₄ .CH ₃	93
8.	4-H ₃ CO.C ₆ H ₄ .CHO	4-H ₃ CO.C ₆ H ₄ .CH ₃	96
9.	4-(H ₃ C) ₂ N-C ₆ H ₄ .CHO	4-(H ₃ C) ₂ N-C ₆ H ₄ .CH ₃	98
10.	3-H ₃ CO-4-OH.C ₆ H ₃ .CHO	3-H ₃ CO-4-OH.C ₆ H ₃ CH ₂ OH	78
11.	2,4-(H ₃ CO) ₂ .C ₆ H ₃ .CHO	2,4-(H ₃ CO) ₂ C ₆ H ₃ CH ₂ OH	82

^a Yield of pure, isolated products.

was dried with anhydrous sodium sulphate and removed under reduced pressure to provide pure products in excellent yield. The results are summarized in Table 1.

Acknowledgment. We thank Principal V.G. Kasbekar, Prof. R.S. Mali and Prof. S.R. Jagtap for their encouragement.

References and Notes

1. Solid Supported Reactions Part 3. For part 2 see: Bandgar, B.P.; Shrotri, N.S.; Ghorpade, P.K.; Patil, S.V. *Indian J. Chem.Sec.B* **1994** (in press).
2. Martin, E.L. *Org.React.* **1942**, 1,155.
3. Todd, D. *Org.React.* **1948**, 4,378.
4. Ram, S.; Spicer, L.D. *Tetrahedron Lett.* **1988**, 29,3741.
5. Petit, G.R.; van Tamen, E.E. *Org.React.* **1962**, 12,356.
6. Olah, G.A.; Wu, A. *Synlett.* **1990**, 54.
7. Ranu, B.C. *Synlett.* **1993**, 12,885 and references cited therein.
8. Gibson, H.W.; Bailey, F.C. *J. Chem. Soc., Chem. Commun.* **1977**, 815.
9. Yoon, N.M.; Park, K.B.; Gyoung, Y.S. *Tetrahedron Lett.* **1983**, 24,5367.
10. Gyoung, Y.S.; Yoon, N.M.; Jeon, D.H. *Bull. Korean Chem. Soc.* **1987**, 8,62.
11. Kabalka, G.W.; Wadgaonkar, P.P.; Chatla, N. *Synth. Commun.* **1990**, 20,293.
12. Chen, J.W.; Qin, C.Q. *Reactive Polymers* **1991/1992**, 16,287.
13. Yoon, N.M.; Choi, J. *Synlett.* **1993**, 135.
14. Yoon, N.M.; Choi, J.; Shon, Y.S. *Synth. Commun.* **1993**, 23,3047.
15. Yoon, N.M.; Cho, J.; Shon, Y.S. *Bull. Korean Chem. Soc.* **1993**, 14,543.

(Received in the UK 11 July 1994)