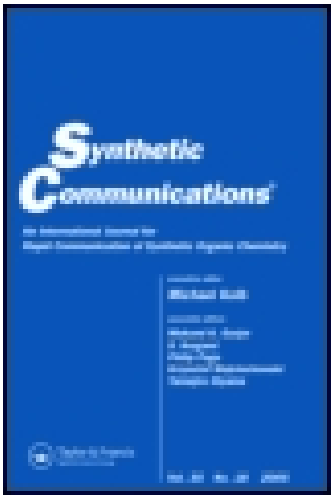

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The Reduction of Aromatic Aldehydes to Hydrocarbons with Borohydride Exchange Resin (BER)-Nickel Acetate in Methanol

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THE REDUCTION OF AROMATIC ALDEHYDES TO HYDROCARBONS WITH BOROHYDRIDE EXCHANGE RESIN (BER)-NICKEL ACETATE IN METHANOL[1]

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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 Clemmensen[2] and Wolf-Kishner reductions[3] several reagents have been developed for the reduction of aromatic aldehydes to the corresponding hydrocarbons.[4-7] Borohydride exchange resin (BER) an useful reducing reagent[8] 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] azides[14] and aryl halides.[15]

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We now wish to report the conversion of ArCHO to $ArCH_3$ using BER-$Ni(OAc)_2$ in methanol (scheme). With this reducing system

$$ArCHO \xrightarrow[Methanol]{BER\text{-}Ni(OAc)_2} ArCH_3$$

simultaneous dechlorination of aryl halide (entry 4) and reduction of nitro group to the amino grpup (entry 5) took place. The reduction of less reactive aromatic aldehydes (entries 10,11) to the corresponding hydrocarbons did not occure 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 conditins 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 $CDCl_3$ 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 BH_4^- 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 filteration. 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_6H_4.CHO	1,4-$(CH_3)_2C_6H_4$	92
4.	4-Cl.C_6H_4.CHO	Ph-CH_3	95
5.	3-NO_2-C_6H_4.CHO	3-NH_2-C_6H_4.CH_3	97
6.	2-OH.C_6H_4.CHO	2-OH.C_6H_4.CH_3	98
7.	3-H_3CO.C_6H_4.CHO	3-H_3CO.C_6H_4.CH_3	93
8.	4-H_3CO.C_6H_4.CHO	4-H_3CO.C_6H_4.CH_3	96
9.	4-$(H_3C)_2N$-C_6H_4.CHO	4-$(H_3C)_2N$-C_6H_4.CH_3	98
10.	3-H_3CO-4-OH.C_6H_3.CHO	3-H_3CO-4-OH.$C_6H_3CH_2OH$	78
11.	2,4-$(H_3CO)_2$.C_6H_3.CHO	2,4-$(H_3CO)_2C_6H_3CH_2OH$	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.

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