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Chemoselective reduction of nitroaromatics to anilines using decaborane in methanol

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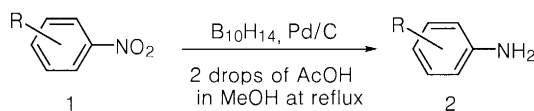
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Abstract

Nitrobenzenes were chemoselectively reduced to the corresponding anilines using decaborane ($B_{10}H_{14}$) in the presence of Pd/C and two drops of acetic acid at reflux under nitrogen atmosphere in high yields. © 1999 Elsevier Science Ltd. All rights reserved.

Aromatic amines are important intermediates for dyes, agricultural, and pharmaceutical chemicals.¹ Most of these aromatic amines are prepared by the reduction of the corresponding nitro aromatics using a metallo hydride reagent or catalytic hydrogenation.² However, these reaction conditions are incompatible with other sensitive functional groups such as nitriles, carbonyl groups, halides and the benzyl-protecting group. Recently, selective reagents for this transformation were developed and reported. These are indium– NH_4Cl in ethanol,³ Sm metal–iodine in methanol,⁴ *N,N*-dimethylhydrazine/ferric chloride,⁵ hydrazine hydrate/ Fe_2O_3 – MgO ,⁶ Diethyl chlorophosphite,⁷ and $NaBH_4$ – $NaOMe$ in methanol.⁸ These methods still have limitations, such as long reaction time, nucleophilic attack (hydrazine), by-products, and/or low yield.

Here, we report an efficient and chemoselective method for reducing nitroaromatics to the corresponding anilines (Scheme 1).⁹ The nitro groups of nitroaromatics were chemoselectively reduced in high yields to the corresponding anilines using decaborane in the presence of 10% Pd/C and two drops of acetic acid in methanol at reflux.



Scheme 1.

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The reduction reaction was attempted under several reaction conditions (Table 1). When the reaction was tried using decaborane at room temperature in methanol, the reaction was slow and in some cases required additional decaborane to reach completion.⁹ When the reaction mixture was heated to reflux, the reaction was fast. However, the irreversible formation of the amine-decaborane adduct was observed¹⁰ and the reaction again required additional decaborane for complete reduction.¹¹ To avoid the formation of these adducts and to increase the rate of the reaction, two drops of acetic acid were added and the reaction was heated at reflux. Under these conditions, the reaction was completed in several hours and gave the corresponding anilines chemoselectively in high yields. Other functional groups such as carbonyls (entries 1, 2, 3 and 4), esters (entries 2 and 3), halide (entry 6), nitrile (entry 8), or the benzyl groups (entries 3 and 9) survived under the reaction condition.

Table 1
Reduction of nitroaromatics using decaborane in methanol

Entry	Substrate (1)	Time (h)	Product (2) ^a	Yield ^b (%)
1	4-Nitrobenzoic acid	<0.5	4-Aminobenzoic acid	97%
2	Methyl 4-nitrobenzoate	0.5	Methyl 4-aminobenzoate	96%
3	Benzyl 4-nitrobenzoate	<1	Benzyl 4-aminobenzoate	91%
4	<i>N</i> -(4-Nitrophenyl)acetamide	<0.5	<i>N</i> -(4-Aminophenyl)acetamide	96%
5	Nitrobenzene	1.5	Aniline	90%
6	2-Bromo-5-nitrotoluene	<0.5	4-Bromo-3-methylaniline	81%
7	4-Nitrotoluene	<1.5	<i>p</i> -toluidene	91%
8	4-Nitrophenylacetonitrile	2.5	4-Aminophenylacetonitrile	95%
9	3-Nitrobenzylalcohol	3	3-Aminobenzylalcohol	94%

a) All products are known compounds and gave spectra (GC-MS, ¹H NMR, IR) and mps consistent with the assigned structures. b) Isolated yields.

In conclusion, nitro groups of nitroaromatics in methanol were chemoselectively converted into the corresponding amines using decaborane in the presence of 10% Pd/C and two drops of acetic acid at reflux under nitrogen in high yields. We observed chemoselectivity in the presence of other functional groups such as ester, bromo, nitrile, amide and benzyl group.

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9. A representative run (entry 3) is as follows: To a solution of benzyl 4-nitrobenzoate (50 mg, 0.276 mmol) in methanol (5 ml) was added decaborane (10 mg), two drops of acetic acid and 10% Pd/C (15 mg). The resulting solution was stirred at reflux under nitrogen for 0.5 h. The reaction was followed by TLC using a solution of ethyl acetate and *n*-hexane (1:2). The mixture was concentrated under reduced pressure, chromatographed on a short pad of silica gel using a solution of ethyl acetate and *n*-hexane (1:4) to give benzyl 4-aminobenzoate as a pale yellow solid.
10. The R_f value of the adduct was higher than that of the corresponding amine according to TLC when a mixture of ethyl acetate and *n*-hexane (1:4) was used as the developing solvent.
11. The starting nitroaromatics remained even after stirring for 2 days or longer. After stirring for 2 days, all of the decaborane was consumed.