

Rapid, efficient and selective reduction of aromatic nitro compounds with sodium borohydride and Raney nickel

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Abstract

A new efficient, mild and practical method for reduction of aromatic nitro compounds employing NaBH₄/Raney nickel system is reported. The method is simple, inexpensive, easily scaled-up and applicable for large scale preparation of different substituted anilines as well as other heterocyclic aryl amines.

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1. Introduction

The reduction of aromatic nitro compounds to corresponding anilines is one of the most important transformations in synthetic organic chemistry. The availability of nitroaromatic compounds, easily prepared by nitration [1] of simple aromatic compounds, allows the shortest and easiest way for synthesis of substituted anilines, which usually serve as starting material in synthesis of other important industrial products such as dyes, pharmaceuticals, agrochemicals etc. Furthermore, amino group can easily be replaced with other groups (H, F, Cl, Br, I, OH, etc.) via corresponding diazonium salts [2].

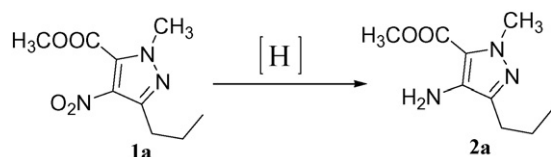
A vast variety of reagents have been used for reduction of nitroaromatic compounds to corresponding anilines. Among them traditional and still important is reduction with iron and hydrochloric or acetic acid [3]. Other dissolving metals such as Zn [4] and Sn [5] in the presence of hydrochloric acid, as well as Zn/NH₃ [6], Sm [7], In [8], activated iron [9], Zn/NaOH/EtOH [10], Al/NH₄Cl/MeOH [11], Zn/CaCl₂/EtOH [12], Co₂(CO)₈/H₂O [13], Mo(CO)₆ [14] have also been used. Other reagents such as SnCl₂/H₂O [15], SnCl₂/ionic liquid [16], N₂H₄/FeCl₃ [17], N₂H₄/Zn [18], TiCl₃ [19], NaHPO₂/FeSO₄ [20], B₁₀H₁₄/Pd/C [21], FeCl₃/Zn/DMF/H₂O

[22], HCOONH₄/Pd/C [23], HCOONH₄/Mg [24], hydrazinium monoformate/Zn [25], N₂H₄/Ru(bpy)₂/hν [26], HCOOH/Raney nickel [27], N₂H₄/Raney nickel [28], HCOONa/K₃PO₄ [29], N₂H₄/AlH₃/AlCl₃ [30], electrochemically generated nickel [31], HCOONH₄/Ni[P(OPh₃)₄] [32], N₂H₄-H₂O/Fe₂O₃/MgO [33], Sm(0)/1,1'-dioctyl-4,4'-bipyridinium dibromide [34] and very recently Zn in the presence of poly[N-(2-aminoethyl)acrylamido]-trimethylammonium chloride [35] and Na₂S/NEt₄Br [36] have also been used. The catalytic hydrogenation employing molecular hydrogen and catalysts such as Pd/C [37], Pd(II) complexes/γ-Al₂O₃ [38], or Raney nickel [39] is one of the most economical and effective methods, particularly for industrial processes due to the fact that no side products, except water, are formed in the reaction. However, the main drawbacks of all these methods are lack of selectivity, water sensitivity and expensiveness of some of the reagents mentioned. When using catalytic hydrogenation, presence of highly flammable molecular hydrogen and high pressures imposes significant risk, not to mention the high price of the equipment. There is also a considerable issue of heat removal on industrial scale. Therefore, development of more selective, fast and practical method for reduction of nitro to amino group is still demanded.

2. Results and discussion

During the attempts of 4-amino-1*N*-methyl-5-methoxy-carbonyl-3*n*-propylpyrazole (**2a**) synthesis (Scheme 1) from

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corresponding 4-nitro-1*N*-methyl-5-methoxycarbonyl-3-*n*-propylpyrazole (**1a**) we have found catalytic hydrogenation with 10%Pd/C as catalyst in ethylacetate or ethanol at room temperature to be very effective method (Table 1, entry 1), but poisoning of the catalyst after few regeneration steps arose as the main problem. The literature method for synthesis of **2a** employing molecular hydrogen and Raney nickel as catalyst require 25 bar hydrogen pressure (Table 1, entry 2) and the crude product is isolated only in 82% yield [40] which is not acceptable for industrial purposes.

Therefore, we decided to test other methods which could potentially be used for commercial synthesis of amino-pyrazole **2a**. Due to acid sensitivity of starting nitro compound **1a** we decided to use hydrazine hydrate as well as ammonium formate as reducing agents in the presence of appropriate catalyst, according to literature methods, Table 1. Unfortunately, no reaction was observed with HCOONH₄/10%Pd/C (entry 3) HCOONH₄/Mg (entry 4) and hydrazinium monoformate/Zn (entry 5). The method employing hydrazine hydrate and Zn (entry 6) efficiently reduces nitro group but hydrazinolysis of ester group is side reaction that could not be prevented. Similarly, N₂H₄·H₂O/Pd/C/EtOH (entry 8) and Et₃N·HCOOH/Pd/C (entry 9) were not selective enough to give **2a** in reasonable yield. Then, we looked at the other hydrogen sources such as sodium borohydride. Considering the fact that NaBH₄ alone does not reduce nitro group, some authors have efficiently used it in the presence of catalysts such as NiCl₂ [41], (py)₃RhCl₃ [42], Cu(II) acetylacetonate [43], Pd/C [44] and phthalocyanatoiron(II) [45]. The products were usually isolated in moderate to good yields but working with homogenous heavy metal catalysts (except Pd/C [44]) makes this method unacceptable for industrial purposes. The attempt to reduce **1a** to **2a** employing NaBH₄ with Pd/C as catalyst in methanol–water mixture as solvent afforded product in only 60% yield after chromatographic purification (Table 1, entry 7). Thus, we decided to test Raney nickel as inex-

pensive heterogeneous catalyst in reduction of nitro-pyrazole (**1a**) with sodium borohydride as hydrogen source.

Herein, we wish to report the results from our investigation that led to the development of new, practical and efficient approach to reduction of aromatic nitro compounds to corresponding anilines.

The first attempt was reduction of compound **1a** in THF as a solvent similarly to conditions used with Pd/C [44] but reaction was very slow and without practical importance. On the other hand, reaction in methanol proceeded smoothly and was completed within 10 min. using only two equivalents of sodium borohydride (Scheme 1). After completion of the reaction, the amine (**2a**) was isolated in 90% yield, Table 1 (entry 10). Monitoring of the reaction by TLC showed formation of few intermediates (less and more polar than starting nitro compound) that all disappeared at the end of the reaction. When the reaction was carried out without catalyst load, only formation of reduction intermediates was observed, without traces of amine (**2a**) even with large excess of NaBH₄. This observation suggests an additional activation of *in situ* formed molecular hydrogen on the surface of Raney nickel, thus, allowing complete reduction.

The replacement of methanol with other alcohols such as ethanol, 2-propanol, *tert*-butanol, etc. led to drastic increase of reaction times and formation of reduction intermediates rather than the amine. The optimal catalyst load (Raney nickel) showed to be 10 mol% and no improvement was observed with higher loads. The catalyst was easily regenerated from reaction mixture by filtration (**CAUTION!** Dry Raney nickel is highly flammable and need to be stored under distilled water). It maintained its activity even after five subsequent reactions.

To explore the scope and limitations of this method we decided to test it on a series of nitroaromatic compounds (entries 1–13). The results presented in Table 2 indicate the generality of the method and efficacy of this new reduction system.

The main characteristics of the reaction are short reaction times (5–20 min), excellent yields (>85%) and high purity of crude products. This method was successfully applied to reduction of simple nitroaromatics such as nitrobenzene (**1c**), substituted aromatics **1d–1k** as well as heterocyclic nitro compounds **1a,b** and **1l**. Many functional groups (COOCH₃, CONH₂, COOH, Cl and Br) including heterocyclic systems are well tolerated except carbonyl group which has been reduced selectively to corresponding alcohol (entry 8). Of particular

Table 1
Reduction of 4-nitro-1*N*-methyl-5-methoxycarbonyl-3-*n*-propylpyrazole (**1a**) with various reducing agents

Entry	Reducens	Time (h)	Yield (%)	Reference
1	10%Pd/C/H ₂ (g)/EtOAc/50 °C	10	93%	[37b,c]
2	Raney nickel/H ₂ (g)	2.5	82	[40]
3	HCOONH ₄ /10%Pd/C	24	No reaction	[23]
4	HCOONH ₄ /Mg	24	No reaction	[24]
5	N ₂ H ₄ ·HCOOH/Zn	24	No reaction	[25]
6	N ₂ H ₄ ·H ₂ O/Zn	0.1 (6 min)	Decomposition	[18]
7	NaBH ₄ /Pd/C/MeOH-H ₂ O	24	60	[48]
8	N ₂ H ₄ ·H ₂ O/Pd/C/EtOH	24	Non-selective	[30]
9	Et ₃ N·HCOOH/Pd/C	12	Non-selective	[46]
10	NaBH ₄ /Raney nickel/MeOH	0.17 (10 min)	90	This article

Table 2

Reduction of aromatic nitro compounds employing sodium borohydride and Raney nickel $\text{Ar} - \text{NO}_2 \xrightarrow[\text{MeOH, 30–40}^\circ\text{C}]{\text{NaBH}_4 \text{ 2.0 equiv. Raney nickel 10 mol\%}} \text{Ar} - \text{NH}_2$

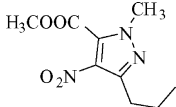
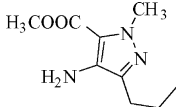
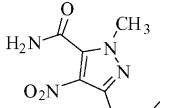
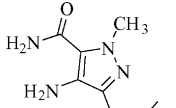


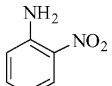
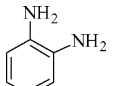
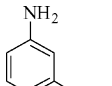
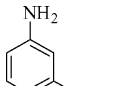


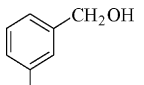
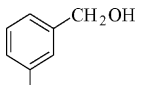
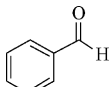
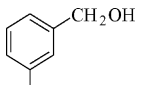


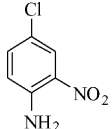
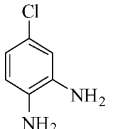
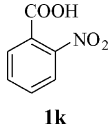
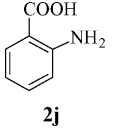
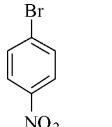
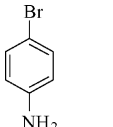
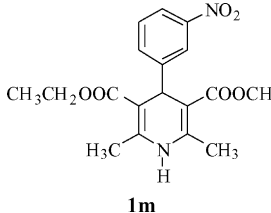
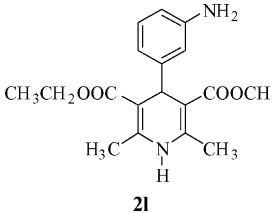
Entry	Nitro compound	Product	Time (min) ^a	Yield (%) ^b
1	 1a	 2a	10	90
2	 1b	 2b	20	87
3	 1c	 2c	5	95
4	 1d	 2d	5	94
5	 1e	 2e	10	95
6	 1f	 2f	10	97
7	 1g	 2g	10	87
8	 1h	 2g	10	85
9	 1i	 2h	10	96

Table 2 (Continued)

Entry	Nitro compound	Product	Time (min) ^a	Yield (%) ^b
10	 1j	 2i	15	92
11	 1k	 2j	20	90
12	 1l	 2k	15	99
13	 1m	 2l	20	85

^a The reaction time was determined by TLC analysis.

^b All products were characterized by ¹H NMR, ¹³C NMR and IR spectra and compared with authentic samples.

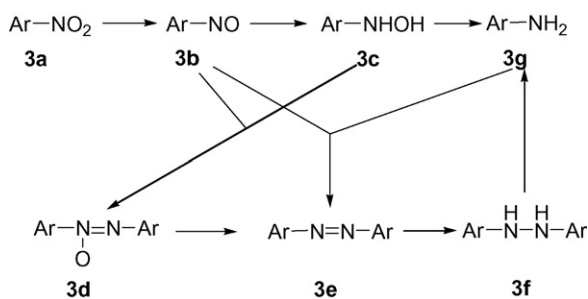
importance is the tolerance to bromine substituent on aromatic ring (**1l**, entry 12) contrary to method employing Pd/C [44] as catalyst as well as recently developed method with S₈/mild base [48], where debromination and decomposition take place.

In all cases, the presence of several less and more polar reaction intermediates is observed that all disappear at the end of the reaction. Therefore, it is proposed that reduction of nitro group with NaBH₄/Raney nickel system involve formation of nitroso (**3b**), hydroxylamino (**3c**), azoxy (**3d**), diazo (**3e**) and hydrazino (**3f**) intermediates, Scheme 2.

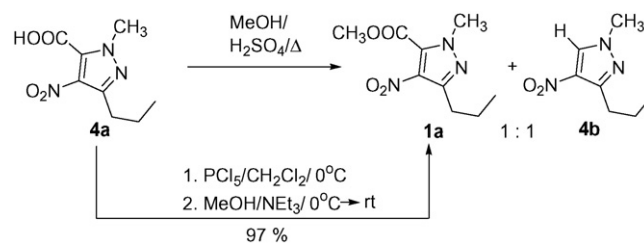
The formation of these intermediates is often observed with many other reducing agents [16,34,47] and in some cases it is possible to isolate them as a sole products [47]. When the reduction with NaBH₄/Raney nickel system is carried out at lower temperature (0–10 °C) it is possible to detect (TLC analy-

sis) some of them, especially nitroso (**3b**), hydroxylamino (**3c**) and diazo (**3e**) intermediates. As the reaction proceeds only final product (**3g**) is observed. This was additionally proved by independent experiments using nitrosobenzene, diazobenzene, hydroxylaminobenzene and azoxybenzene as substrates. In all cases selective formation of aniline (**2c**) is observed suggesting their existence as intermediates in nitro group reduction.

In addition, we decided to study the possibility of scaling up this new reduction system. Firstly, more practical and scalable method for synthesis of starting nitroester **1a** was needed. For lab. studies, starting from commercially available nitroacid **4a**, **1a** was prepared in one step reaction in only 50% yield after chromatographic purification. Significant formation of decarboxylation product **4b** was observed in acid catalysed esterification, Scheme 3. We believe that side products are formed due to slower esterification step compared to decarboxylation of thermodynamically unstable nitro acid **4a**. To prevent unwanted side



Scheme 2.



Scheme 3.

reaction corresponding acid chloride was prepared at mild conditions employing phosphorus pentachloride in dichloromethane which was converted to ester **1a** in almost quantitative yield, Scheme 3.

This method was easily scaled-up and served for synthesis of **1a** at a kilogram scale. Thus, following the same procedure as on the lab. scale, reduction of **1a** was carried out on 5 kg scale in a 100 L vessel equipped with cooling system. Due to a slower heat removal comparing to the lab. conditions, sodium borohydride was charged during 60 min. and additional 60 min of reaction time was required for reaction to complete. Yield of crude product **2a** was even slightly higher (92%) comparing to lab. scale (90%), and chemical purity also maintained high.

The presented results illustrate the scope and efficiency of this new reduction system for the selective reduction of aromatic nitro compounds to corresponding anilines in mild conditions. We believe that this method is important addition to known procedures for reduction of aromatic nitro compounds either on a lab. as well as on larger scale. Use of Raney nickel as heterogeneous catalyst allows its efficient regeneration and, thus, the product is free of heavy metal contrary to homogenous type of catalysis [26,32,37,42,43,45].

Aromatic nitro compounds can be efficiently and selectively reduced to corresponding anilines employing sodium borohydride and Raney nickel catalytical system in methanol at mild condition. The reaction is fast and the products are isolated in good to excellent yields.

3. Experimental

3.1. General

IR spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a AV Bruker (600 MHz) spectrometer, and shifts are given in ppm downfield from TMS as an internal standard. TLC analyses were performed on Merck's (Darmstadt, Germany) DC-alufolien with Kieselgel 60F₂₅₄. Melting points were determined using a Büchi B-540 instrument.

3.2. Synthesis of

4-nitro-1*N*-methyl-5-methoxycarbonyl-3*n*-propylpyrazole (**1a**)

To a suspension of 4-nitro-1*N*-methyl-3*n*-propylpyrazole-5-carboxylic acid (**1a**, 100.00 g, 0.469 mol) in dichloromethane (500 mL) cooled to 10–15 °C, phosphorus pentachloride (100 g, 0.480 mol, 1.02 equiv.) was added in a few portions during 30 min. The reaction mixture was then spontaneously heated to room temperature and stirred for additional 4 h. After cooling to 10 °C to the reaction mixture was added solution of triethylamine (100 mL, 73.00 g, 0.721 mol, 1.5 equiv.) in methanol (60 mL, 1.48 mol, 3 equiv.) by keeping the temperature below 15 °C. After stirring at room temperature for 2 h, to the reaction mixture was added water (400 mL) at about 25 °C and stirring was continued for 30 min. After separation of layers, water layer was additionally extracted with dichloromethane

(2 mL × 100 mL). Combined organic layers were dried over anhydrous Na₂SO₄, filtered and evaporated to dryness to afford crude product **1a** (HPLC purity >99%) as a brown crystals; mp 47.5–50.0 °C; yield 103.82 g (97.4%). The analytical sample was purified by preparative chromatography on silica column with dichloromethane as eluents. The fractions with *R*_f 0.38 were collected and evaporated to dryness to give pure **1a** as a yellow crystals; mp 50.8–53.1 °C; found: C, 47.4; H, 5.6; N, 18.6. C₉H₁₃N₃O₄ requires C, 47.57; H, 5.77; N, 18.49; ν_{max} (KBr) 1728, 1558, 1502, 1294 cm⁻¹; δ_{H} (600 MHz, DMSO-*d*₆) 3.95 (3H, s, OCH₃), 3.93 (3H, s, NCH₃), 2.76 (2H, t, *J*=7.5, CH₂CH₂CH₃), 1.64 (2H, q, *J*=14.9, CH₂CH₂CH₃), 0.92 (3H, t, *J*=7.5, CH₂CH₂CH₃); δ_{C} (600 MHz, DMSO-*d*₆) 158.79, 147.78, 132.43, 131.54, 53.81, 39.06, 28.11, 20.82, 13.56.

3.3. General procedure for the reduction of nitroaromatics **1a–1m**

To a solution of nitroaromatics **1a–1m** (10 mmol) in methanol (20 mL) Raney nickel (59 mg, 10 mol%) was added at room temperature. After that sodium borohydride (0.76 g, 20 mmol, 2 equiv.) was slowly and carefully added in a few portions by keeping the temperature between 30 and 40 °C with external cooling. The reaction mixture was stirred for the time indicated in Table 1. The catalyst was filtered off, washed with methanol (5 mL) and immediately immersed in distilled water to prevent spontaneous combustion. The filtrate was evaporated to dryness and the residue was partitioned between water (20 mL) and dichloromethane (20 mL). After separation of the phases, water layer was additionally extracted with dichloromethane (2 mL × 10 mL). Combined organic extracts were dried over anhydrous Na₂SO₄, filtered and evaporated to dryness to afford pure products whose purities according to ^1H NMR were generally >98%. Analytical results (IR, ^1H , ^{13}C NMR) of known products **2b** [49], **2c**, **2d–2g** [25], **2h** [25], **2i**, **2j** [25] and **2k** [25] were identical to those reported in literature or commercially available material.

2a-red oil; bp 285.0–290.0 °C; found: C, 54.6; H, 7.5; N, 21.2. C₉H₁₅N₃O₂ requires C, 54.81; H, 7.67; N, 21.30; ν_{max} (film) 3459, 3366, 1713, 1614, 1557, 1521, 1287, 1231, 1192, 1143 cm⁻¹; δ_{H} (600 MHz, DMSO-*d*₆) 4.79 (2H, s, NH₂), 3.85 (3H, s, OCH₃), 3.80 (3H, s, NCH₃), 2.41–2.46 (2H, m, CH₂CH₂CH₃), 1.55 (2H, q, *J*=14.9, CH₂CH₂CH₃), 0.89 (3H, t, *J*=7.5, CH₂CH₂CH₃); δ_{C} (600 MHz, DMSO-*d*₆) 161.36, 138.05, 135.97, 116.27, 51.52, 39.60, 27.08, 21.62, 14.18.

2l-colourless crystals; mp 169.5–172.0 °C; found: C, 65.2; H, 6.5; N, 8.3. C₁₈H₂₂N₂O₄ requires C, 65.44; H, 6.71; N, 8.48; ν_{max} (film) 3458, 3343, 1662, 1601, 1485, 1321, 1221, 1130, 1018 cm⁻¹; δ_{H} (600 MHz, CDCl₃) 6.93 (1H, t, *J*=7.3, arom.), 6.63 (1H, d, *J*=7.6, arom.), 6.56 (1H, s, arom.), 6.22 (1H, d, *J*=7.8, arom.), 5.88 (1H, s, NH), 4.88 (1H, s, CH), 4.01–4.10 (2H, m, CH₂CH₃), 3.58 (3H, s, OCH₃), 3.48 (2H, br s, NH₂), 2.25 (3H, s, CH₃) 2.23 (3H, s, CH₃) 1.18 (3H, t, *J*=7.1, CH₂CH₃); δ_{C} (600 MHz, CDCl₃) 167.71, 167.25, 148.15, 145.42, 143.76, 143.41, 128.27, 117.92, 114.37, 112.85, 103.51, 103.11, 59.24, 50.45, 38.78, 19.00, 13.82.

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