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Research Article



Use of Mineral Water as a Co-Catalyst for the Conversion of Toxic Nitro Benzene Derivatives to Aryl Amine Derivatives

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ABSTRACT

A series of toxic nitro compounds were converted to aryl amine derivatives at room temperature in the presence of a hydrogen source such as sodium borohydride and in commercially available mineral water without the need for an organic solvent. A commercial catalyst containing Pd (PdAlO(OH) NPs) was used as the supporting material in the study. However, the amount of catalyst used was reduced by 40% compared to the amounts used previously due to the effect of mineral water. Thanks to the developed environmentally friendly and practical method, 8 different nitro arene compounds were converted to aryl amine derivatives with yields over 95%. The most powerful aspect of the developed method is that it is economical and industrial.

Keywords: Mineral water, Hydrogenation, Aryl amine

Toksik Nitro Benzen Türevlerinin Aril Amin Türevlerine Dönüştürülmesinde Yardımcı Katalizör Olarak Maden Suyunun Kullanımı

ÖZ

Bir dizi toksik nitro bileşiği, organik bir çözücüye ihtiyaç duyulmadan, sodyum borhidrit gibi bir hidrojen kaynağının varlığında ve ticari olarak temin edilebilen maden suyunda oda sıcaklığında aril amin türevlerine dönüştürülmüştür. Çalışmada destekleyici malzeme olarak Pd (PdAlO(OH) NPs) içeren ticari bir katalizör kullanılmıştır. Ancak, kullanılan katalizör miktarı, maden suyunun etkisi nedeniyle daha önce kullanılan miktarlara kıyasla %40 oranında azaltılmıştır. Geliştirilen çevre dostu ve pratik yöntem sayesinde, 8 farklı nitro aren bileşiği %95'in üzerinde verimlerle aril amin türevlerine dönüştürülmüştür. Geliştirilen yöntemin en güçlü yönü, ekonomik ve endüstriyel olmasıdır.

Anahtar Kelimeler: Mineral su, Hidrojenasyon, Aril amin

I. INTRODUCTION

The development of effective methods for reducing or eliminating toxic compounds such as aromatic nitro compounds has gained importance in industrial processes in recent years. One way to transform aromatic nitro compounds is to convert them into aromatic amines [1, 2]. Aryl amines are both important precursor molecules for natural products, organic materials, polymers, fine chemicals and important industrial intermediates [3],[4]. They are widely used as dyes for textiles, drugs, food and cosmetics. Aliphatic amines and their derivatives are useful softeners, wetting agents, dye stabilizers, asphalt emulsifiers, pigment dispersants, petroleum additives, ore flotation agents and additives for cosmetic preparations [5-8]. In addition to these properties of amine derivatives, their biologically active derivatives used as drug molecules are also quite common. For example, cathinone structures have been proven to have an antimicrobial effect as well as a toxic effect [9]. Mescaline is a natural alkaloid and a hallucinogen that has been known for over 5,000 years [10, 11] Adefovir is an antiviral drug used to treat chronic hepatitis B [12].

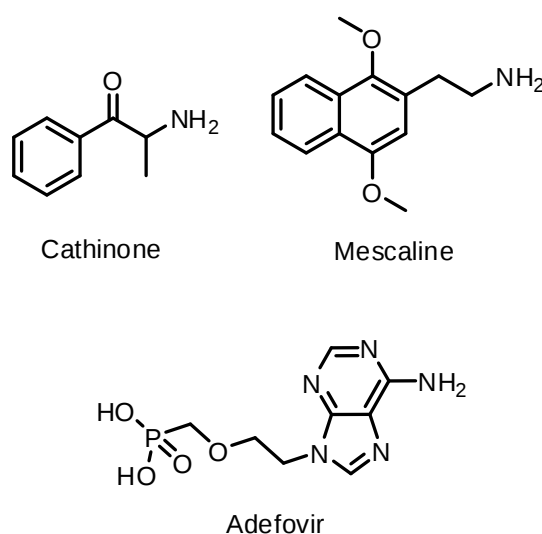


Figure 1. Biologically active compounds containing amino groups

As mentioned before, toxic nitro compounds are commonly converted into aryl amine derivatives, thus minimizing their effects. There are many methods for obtaining aryl amines. However, the most commonly used method is hydrogenation of nitro compounds. Solid, liquid and gaseous hydrogen sources are used in the hydrogenation process. Each source has advantages and/or disadvantages compared to each other. However, solid hydrogen sources are preferred in terms of ease of transportation, storage and application [13-17]. The catalyst systems are used especially for the dehydrogenation of solid hydrogen sources and hydrogenation of nitro compounds. For this purpose, the activity of one or more metal-based catalysts such as Pd[18], Co[19], Fe[20], Cu[21], Raney Ni[22], RuNi[23], Au/Ag[24], Pt/Pd[25] in hydrogenation reactions has been demonstrated by studies. Palladium-containing catalysts are preferred more in terms of efficiency and reusability performance. Commercially available Pd/AlO(OH) nanoparticles (NPs) were first used by the present author group for the effective reduction of nitro compounds to primary amines[26]. In this study, the amount of catalyst used was reduced by 40% with the developed method. In addition, in hydrogenation reactions, the solvent system, as well as the hydrogen source and catalyst, affects the course of the reaction. Organic solvents are generally used in reactions. However, this is contrary to the concept of green chemistry. In methods developed for this purpose, the use of water instead of organic solvents has gained importance in recent years. In particular, the use of mineral water not only provides the use of a local and national resource, but also reveals the catalytic activity of the minerals in it [27-30].

II. MATERIALS AND METHODS

A. MATERIALS

The nitro compounds, PdAlO(OH) NPs and NaBH₄ used in the study were obtained from Sigma-Aldrich. Beypazarı brand mineral water was used in the experiments.

B. METHODS

B.1. Characterization Methods

The NMR spectra were recorded on a AVANCE III 400MHz spectrometer.

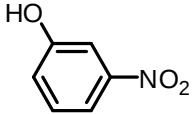
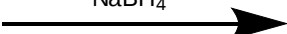
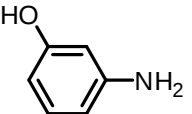
B.2. General Procedure for the Synthesis of Primary Amine Compounds

Into a reaction vessel at room temperature were placed 0.25 mmol of the nitro benzene derivatives, and 15 mg of PdAlO(OH) NPs. 1.0 ml of mineral water was added to the reaction vessel. Afterwards, 0.75 mmol of sodium borohydride was rapidly added to the reaction mixture and the lid of the reaction vessel was tightly closed. The progress of reaction was monitored by TLC analysis. All reactions were completed within 5 minutes. After the reaction was completed, the catalyst was separated by centrifugation and the solvent was removed by evaporator. The products were purified by flash column chromatography and identified by ¹H-NMR and ¹³C-NMR.

III. RESULTS AND DISCUSSION

In the optimization studies, 3-nitrophenol (1f) compound was used as substrate. The reason for preference is that this compound is well soluble in water (26.3 g/L, 20 °C). The experiments were carried out in different solvents, temperatures, times and catalyst amounts. First of all, no product formation was observed in the reaction carried out in toluene, an apolar solvent, and at 110 °C for 4 hours (Table 1, entry 1).

Table 1. Optimization conditions for the synthesis of 3-aminophenol (2f)^a

 1f Mineral water NaBH₄ rt   2f					
Entry	Solvent	Catalyst amount (mg)	Temperature (°C)	Time	Yield ^b (%)
1	Toluene	40	110	4.0 h	-
2	CH ₂ Cl ₂	40	25	4.0 h	-
3 ^c	H ₂ O	25	25	0.7 min	>99
4	H ₂ O	15	25	4.0 min	>95
5 ^c [26]	H ₂ O-MeOH (7:3)	25	25	1.15 min	>99
6 ^d	Mineral water	15	25	2.5 min	>95

^a Reaction Conditions: 0.25 mmol of substrate, 0.75 mmol of NaBH₄, ^b The yield was determined by the analysis of the ¹H NMR spectra. ^cPrevious Study. ^dCurrent Conditions.

No product formation was observed in the reaction carried out in dichloromethane, a polar solvent, at room temperature (Table 1, entry 2). However, it was determined that the expected product was obtained in a much shorter time and with quantitative yields in an environmentally friendly solvent such as water at room temperature (Table 1, entry 3). When the reaction is carried out with only water and 15 mg of catalyst, it is completed in 4 minutes with over 95% efficiency (Table 1, entry 4). By using methanol together with water as solvent, it was possible to develop the procedure that addresses a wider substrate and the reactions took place at room temperature and within 1.15 min with quantitative yields (Table 1, entry 5). When the same experiments were carried out in mineral water, it was determined that the reaction was completed with a lower amount of catalyst (15 mg). Mineral water, which was planned to be used as a solvent, not only carried out the reaction but also supported the use of a lower amount of catalyst (Table 1, entry 6).

Table 2 shows that a series of nitro arenes were reduced under the effect of mineral water and heterogenous catalyst. PdAlO(OH) NPs was used as the heterogenous catalyst and NaBH₄ was used as the reducing material. According to the final procedure obtained as a result of optimization studies, it was determined that aniline derivatives were obtained with a yield of over 95% when 0.25 mmol of substrate, 0.75 mmol of sodium borohydride and 15 mg of PdAlO(OH) NPs were reacted in 1 mL of mineral water at room temperature.

In the method previously developed by our group, 25 mg of PdAlO(OH) NPs were used in water-methanol solvent mixture for the reduction of different structured nitroarenes to aniline derivatives (Table 1, entry 5). Again, in this study, the amount of Pd passing into the solution was found to be 0.1 ppm by ICP-OES analysis and was tolerated because it was below 1%. At the same time, the catalyst was isolated and used again in reactions with high efficiency. EDX, SEM and XRD images of the catalyst before and after the reaction were presented [26]. In a different study developed with the same catalyst, TEM images were also evaluated [31]. In this study, the relevant catalyst was used in lower amounts (15 mg) with the effect of mineral water, and high efficiency was demonstrated. The Pd content used and its solubility in the area of use are important parameters that reveal the toxicity of the catalyst. Moreover, it has been revealed by the studies that toxicity is not only a feature coming from metals. On the other hand, these parameters affect the greenness and sustainability of the method developed [32-34].

Table 2. The reduction of nitro arenes in the presence of mineral water ^a

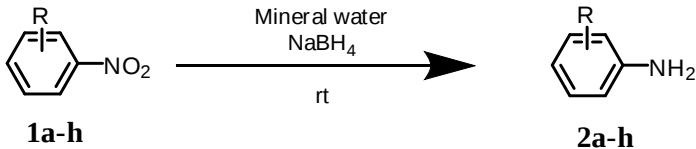
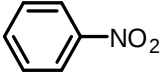
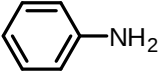
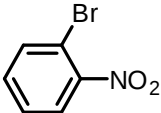
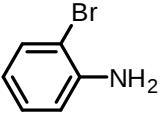
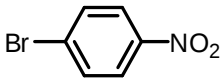
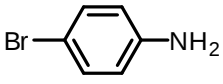
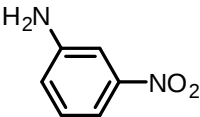
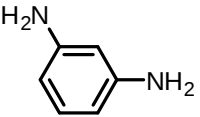
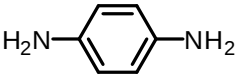
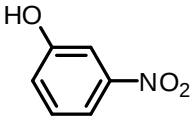
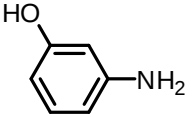
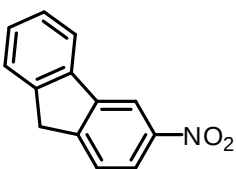
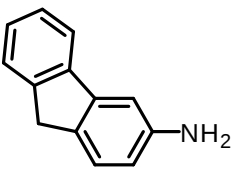
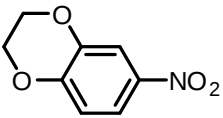
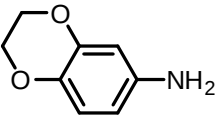
				
Entry	Substrate	Product	Time, (min)	Yield ^b (%)
1			5	>95
2			5	>95
3			5	>95

Table 2 (cont) . The reduction of nitro arenes in the presence of mineral water ^a

4			5	>95
	1d	2d		
5			5	>95
	1e	2e		
6			5	>95
	1f	2f		
7			5	>95
	1g	2g		
8			5	>95
	1h	2h		

^aUnless otherwise stated, 0.25 mmol of substrate, 0.75 mmol of NaBH₄, 15 mg of PdAlO(OH) NPs (0.5 wt% Pd), 1.0 mL of mineral water, at room temperature, ^bAll products are known compounds and exhibit satisfactory spectroscopic data.

In the developed method, a reductant such as sodium borohydride was used in an amount of 3 eq. compared to the nitro benzene derivatives. In addition, mineral water was used as a solvent and co-catalyst in the reaction. The main catalyst role was assumed by PdAlO(OH) NPs [26].

Metal ions such as Fe²⁺, Mg²⁺, Ca²⁺, Na⁺, K⁺, ionic structures such as bicarbonate, sulfate, chloride, fluoride and pH level contained in mineral water contribute to reduction reactions. Redox active metal ions such as Fe²⁺ act as electron donors in reduction reactions.[35, 36] It contributes to the reduction of nitro compounds in acidic conditions. The pH of the environment is important. Acidic conditions are advantageous for reduction reactions[37]. Trace amounts of ions such as Cu²⁺ and Mn²⁺ participate in redox cycles and show a catalytic effect. Of course, the concentration of such ions is important for activity[38]. In the purification of water polluted with nitro compounds, reduction reactions are carried out by means of ions found in mineral water. In order to continue with mineral water alone, the mineral content must be enriched. The mineral values of the mineral water used in the study are fixed and the amount we use is certain. Therefore, it would be more meaningful to use these systems with an additional reducing system or catalyst[39, 40].

Based on the starting material, the reactions were completed in less than 5 minutes. However, since the reduction of 6-nitro-2,3-dihydrobenzo[b][1,4]dioxine was completed in 5 minutes, the duration of the other reactions was also extended to 5 minutes.

It was initially planned not to use a metallic catalyst within the scope of the study. However, as a result of the experiments, it was revealed that the mineral water used did not fully catalyze the reaction. For this purpose, a metallic catalyst was needed. The catalyst used in the study was previously used by our group. However, the amount used in the relevant study was reduced and used in this study. The most important factor in reducing the amount of metallic heterogeneous catalyst was mineral water. The minerals in the mineral water initiated the reduction reaction.

When sodium borohydride is added to the reaction, instantaneous heating occurs. In fact, an instantaneous increase in the reaction temperature also increases the solubility of the nitro compounds used as starting compounds in water. Nitro compounds with increased solubility are rapidly reduced and converted into amino groups with better solubility in water than the starting compound, and the reaction is rapidly completed with this cycle. The products formed, namely compounds containing amino groups, increase their stability in the water phase by hydrogen bonding with water.

IV. CONCLUSION

As a result, 8 different nitro benzene derivatives were converted to aryl amine derivatives with quantitative yields under the influence of a reductant such as sodium borohydride, a catalyst such as PdAlO(OH) NPs and mineral water used as both co-catalyst and solvent. All products obtained were identified with ^1H and ^{13}C NMR spectra. There is an important result obtained with the developed method that the solubility of the selected substrates in water significantly affects the reaction yield. In addition, the amount of heterogeneous catalyst used was reduced due to the fact that mineral water also has a catalytic effect. With an environmentally friendly, economical and practical method, nitro benzene derivatives were converted to aryl amine derivatives in a short time and with high yields.

Article Information

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