

## 수소첨가 촉매 반응에 의한 니트로 화합물에서 방향족 1차 아민을 제조하는 편리한 방법

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### A Convenient Method for the Catalytic Hydrogenation of Aromatic Nitro Compounds to Aromatic Primary Amines

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#### 요 약

방향족 니트로 화합물들을 10% Palladium 촉매 존재 하에서 벤젠 용액에서 45 psi의 압력을 가지고 실온에서 수소첨가 반응시켜서 방향족 아민들을 얻었다. 본 연구에서는 방향족 니트로 화합물로서

nitrobenzene-d<sub>5</sub>, <sup>15</sup>N-nitrobenzene, 그리고 4'-nitrobenzo-15-crown-5를 이용하여 수소첨가 반응을 통하여 방향족 아민들을 합성하였다. 적외선 흡수 스펙트럼에서 수소첨가 반응으로부터 얻어진 아민에서 특성적인 N-H 신축 진동이 3450과 3350cm<sup>-1</sup>에서 나타났다. 연구결과 수소첨가 촉매 반응에 의하여 방향족 아민 화합물을 제조할 때는 수득률이 양호하고 부 생성물의 생성이 크지 않아 다른 방법으로는 쉽게 제조할 수 없는 방향족 아민 화합물을 상업적으로 제조할 수 있음을 보여주고 있다.

## Abstract

Aromatic primary amines were prepared by the catalytic hydrogenation of aromatic nitro compounds in a benzene solution over 50 mg of 10 % palladium on charcoal at a room temperature under 45 psi. This paper describes a study on the catalytic hydrogenation of nitrobenzene-d<sub>5</sub>, <sup>15</sup>N-labelled nitrobenzene, and 4'-nitrobenzo-15-crown-5, respectively. The infrared absorption spectra exhibited a characteristic N-H stretching vibrations at 3450 and 3350 cm<sup>-1</sup>. The results suggest that the non-readily available aromatic amines would be commercially produced by catalytic hydrogenation because of its good yield and little by-product formation.

## Introduction

A large number of reducing agents have been used to reduce aromatic nitro groups.<sup>(1)</sup> Iron was one of the first metals employed for the reduction of nitro compound.<sup>(2)</sup> The reductions are usually carried out in an aqueous media and require only catalytic amounts of acetic acids. Zinc reduces nitro groups in different ways depending mainly on the pH. The reduction to amino groups can be achieved in aqueous alcohol in the presence of calcium chloride.<sup>(3)</sup> Lithium aluminum hydride reduces aliphatic nitro compounds to amines, but with aromatic nitro compounds the products with this reagent are azo compounds.<sup>(4)</sup> Other common reducing agents are titanium chloride,<sup>(5)</sup> stannous chloride,<sup>(6)</sup> ferrous sulfate,<sup>(7)</sup> hydrogen sulfide,<sup>(8)</sup> iron powder and ammonium chloride.<sup>(9)</sup> Several

reducing agents have been used to reduce nitro compounds, but the range of applicability appears to be limited.

Catalytic hydrogenation has been known to be one of the most convenient method for the reduction of nitro compounds.<sup>(10)</sup> Catalytic hydrogenation is usually an extremely clean reaction for the reduction of complex nitro derivatives with little by-product formation, unless other groups in the compounds are to be reduced competitively. Catalytic hydrogenation is effected by shaking a solution of the nitro compound to be reduced with a palladium catalyst under an atmosphere of hydrogen gas. We wish to report the synthesis the non-readily available aromatic primary amines by catalytic hydrogenation. Application of catalytic hydrogenation in the synthesis of aromatic primary

amines, aniline-d<sub>5</sub>, aniline-<sup>15</sup>N, and 4'-aminobenzo-15-crown-5 were investigated during the course of current study.

## Experimental Section

IR spectra were recorded on a Perkin Elmer 1650 series FT-IR spectrometer between 4000 cm<sup>-1</sup> and 400cm<sup>-1</sup> and their positions are reported in wavenumbers. The <sup>1</sup>H NMR spectra was obtained on an AM-300 Bruker spectrometer. Chemical shifts (δ) are given downfield from internal tetramethylsilane. All chemicals used were commercially available reagent grade.

The aromatic nitro compound (12 mmol) was placed slowly in a Parr shaker bottle together with 50.0 mg palladium catalyst (10 %) and benzene (80 ml), under hydrogen pressure at 45 psi. The bottle was shaken at a room temperature until the pressure remained constant. TLC analysis of the reaction mixture with 20% ethyl acetate in hexane showed complete disappearance of the starting nitro compound and the appearance of a new spot. The reaction solution was filtered with gravity on a fluted

filter paper and the reaction flask and catalyst were washed with additional portions of benzene. The solvent was evaporated and the crude aromatic primary amine purified by column chromatography using 5% ethyl acetate in hexane as the mobile phase.

## Results and Discussion

The aromatic nitro compounds were reduced catalytically in a benzene solution under hydrogen pressure to give the corresponding aromatic primary amines. The amines could be purified by column chromatography on silica quite easily. Nitrobenzene-d<sub>5</sub> **2** was synthesized from benzene-d<sub>6</sub> **1** and nitric acid-d in the presence of a catalytic amount of concentrated sulfuric acid-d<sub>2</sub> as shown in Scheme 1. TLC analysis of the reaction mixture with 20% ethyl acetate in hexane showed complete disappearance of the starting benzene and appearance of a new spot. The nitrobenzene-d<sub>5</sub> **2** was converted to aniline-d<sub>5</sub> **3** by catalytic hydrogenation. The Parr hydrogenation apparatus was used for the hydrogenation at a room temperature under a hydrogen pressure of 45 psi. The reaction was

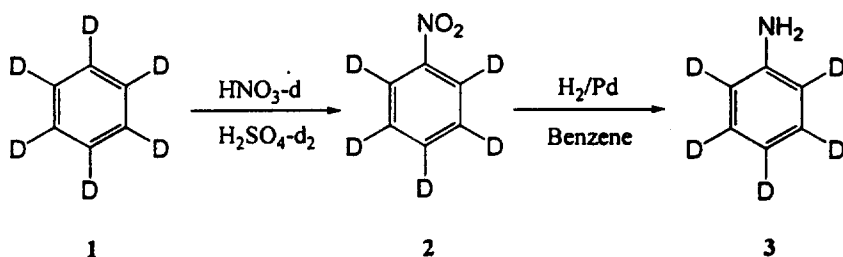


Fig. 1 Catalytic hydrogenation of nitrobenzene-d<sub>5</sub>

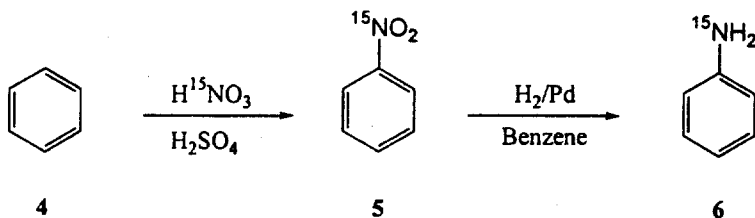
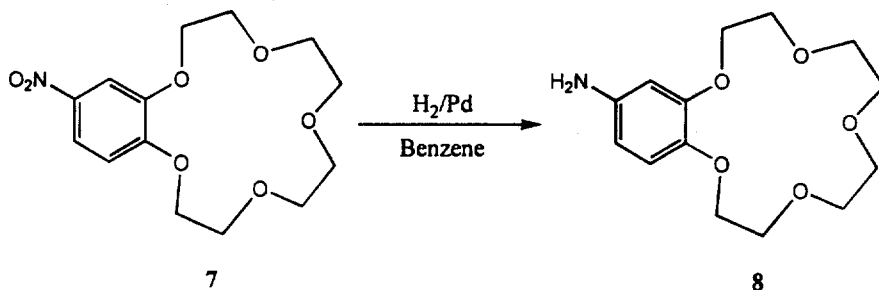
Fig. 2 Catalytic hydrogenation of nitrobenzene- $^{15}\text{N}$ 

Fig. 3 Catalytic hydrogenation of 4'-nitrobenzo-15-crown-5

followed by observing the disappearance of the nitrobenzene using TLC as well as in the infrared absorption spectra where the appearance of the primary amine stretch was clearly evident. The noticeable feature in aniline- $\text{d}_5$  **3** is the appearance of a new band for the primary amine at  $3450$  and  $3350\text{cm}^{-1}$ .

The  $^{15}\text{N}$ -labelled nitrobenzene **5** was prepared from benzene and nitric acid- $^{15}\text{N}$  in the presence of a catalytic amount of concentrated sulfuric acid as shown in Scheme 2. The  $^{15}\text{N}$ -labelled nitrobenzene **5** was reduced to aniline- $^{15}\text{N}$  **6** by catalytic hydrogenation. The reduction of  $^{15}\text{N}$ -labelled nitrobenzene **5** to aniline- $^{15}\text{N}$  **6** proceeded very rapidly at room temperature. The progress of the reduction was followed readily by measuring the uptake of hydrogen. The

aniline- $^{15}\text{N}$  **6** was isolated by filtration of the catalyst followed by evaporation. The reaction mixture was isolated as a liquid in 93% yield by column chromatography purification using 5% ethyl acetate in hexane. In the  $^1\text{H}$  NMR spectrum of aniline- $^{15}\text{N}$  **6**, the amine group appears as a singlet at 3.58 ppm.

4'-nitrobenzo-15-crown-5 **7** was reduced to the 4'-aminobenzo-15-crown-5 **8** by catalytic hydrogenation as shown in Scheme 3. The parr hydrogenation apparatus was used for the hydrogenation at a room temperature under a hydrogen pressure of 45 psi. TLC analysis of the reaction mixture with 20% ethyl acetate in hexane showed complete disappearance of starting nitro compound and appearance of a new spot. Removal of the solvent by rotary evaporation

followed by column chromatography purification using 5% ethyl acetate in hexane as the mobile phase afforded the desired 4'-aminobenzo-5-crown-5 8. Recrystallization from ethyl acetate and hexane gave a pure product.

## Conclusion

The method described here is a convenient way to prepare aromatic primary amines from aromatic nitro compounds. The nitro compounds were easily reduced by catalytic hydrogenation to afford aromatic primary amines in good yields. The Parr hydrogen apparatus was used for catalytic hydrogenation at a room temperature under hydrogen pressure over a palladium catalyst. The reaction was followed by observing the change in pressure in the closed vessel as a function of time. Because the interesting substituents can be varied, this method can lead to a variety of useful aromatic primary amines.

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