Selective Partial Hydrogenation of Dinitrobenzenes to Nitroanilines Catalyzed by Ru/C

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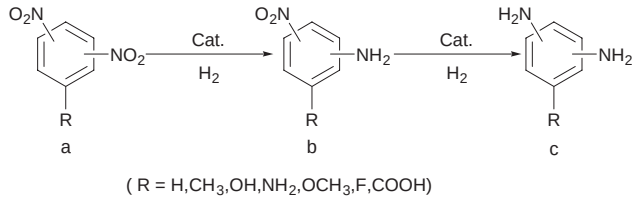
Ru/C was found to be a highly effective catalyst for the selective partial hydrogenation of a range of dinitrobenzenes to their corresponding nitroanilines with excellent selectivity under mild conditions. Furthermore, the effect from other substitute groups of dinitrobenzenes on partial hydrogenation was also explored in this study.

Various nitroanilines are widely used as important intermediates in many chemistry-related industries.[1] Generally, nitroanilines are obtained either from anilines by nitration after acetylation, with subsequent removal of the acetyl group by hydrolysis,[2] or from partial reduction of dinitrobenzenes using sulfide reagents or iron powder.[3] Both two methods are hazardous to the environment and tedious in further separation and waste disposal. For reasons of economy and environment protection, selective catalytical hydrogenation of dinitrobenzenes to obtain nitroanilines has attracted much attention in recent years.[4–8]

During past thirty years, ruthenium-catalyzed processes have become one of the most preferred methodologies in organic synthesis because of their highly efficient performance and versatile applications.[9] For example, Ru-based catalysts are effective in selective hydrogenolysis of glycerol to 1,2-propanediol,[10] ammonia synthesis,[11] and partial selective hydrogenation of benzene to cyclohexene.[12] Very recently, PVP–Ru/Al_2O_3 was discovered to be an effective catalyst for partial hydrogenation of *m*-dinitrobenzene to *m*-nitroaniline in almost 100% yield; however, the Sn^{4+} was added to the catalysis system as modifier, and the study only investigated the hydrogenation of *m*-dinitrobenzene.[13]

Herein, we describe a simple and controllable scheme for selective partial reduction of dinitrobenzenes to corresponding nitroanilines based on a Ru/C-catalyzed process with excellent selectivity. The process involves two steps including the initial hydrogenation of dinitrobenzenes to nitroanilines with high selectivity and subsequent hydrogenation of the nitroanilines to phenylenediamines (Scheme 1).

In the first experiments, Ru/C catalyst was prepared by mixing predetermined quantities of the appropriate homogeneous stock solutions of metal chloride precursors containing Brij35 and Tween 20 as stabilizer, followed by reduction with sodium borohydride under stirring and impregnation of active carbon powder into the solution (See Supporting Information).[14]



Scheme 1. Simplified reaction scheme for the hydrogenation of dinitroaromatics.

Our initial investigation focused on the hydrogenation of *m*-dinitrobenzene (**1a**) using Ru/C catalyst, and the reaction process was monitored by gas chromatography (GC). In accord with Figure 1, GC monitoring of the catalytic reduction of **1a** over Ru/C showed that hydrogenation of *m*-dinitrobenzene was a stepwise reaction, in which the initial hydrogenation step took place readily to afford *m*-nitroaniline (**1b**), which then evolved into the final *m*-phenyldiamine (**1c**) with nearly constant reaction rate. The excellent selectivity to **1b** (>99%) was obtained until **1a** converted completely, while the other nitro group was untouched. Thus, the highest yield to **1b** could be achieved through controlling hydrogen consumption or reaction time.

More importantly, Ru/C was also found to be very efficient in the selective partial hydrogenation of a range of substituted dinitrobenzenes in this study (Table 1), implying the synthetic utility of this catalytic transformation.

As can be seen from Table 1, *m*-, *o*-, *p*-dinitrobenzenes gave corresponding nitroanilines with excellent selectivity under the optimal conditions, indicating the position of two nitro groups had very little effect on the selectivity of partial hydrogenation. Furthermore, for substituted dinitrobenzenes, both electron-donating and electron-withdrawing substituted derivatives could be partially hydrogenated to corresponding nitroanilines with high selectivity (>95%).

It was evident from Table 1 that the existence of electron-withdrawing groups (such as –COOH and –F) could make partial hydrogenation occur more easily when compared to electron-donating substituted dinitrobenzenes (such as –OH, $–NH_2$, $–CH_3$, and $–OCH_3$) in expression of reaction conditions. The facile reduction of electrophilic substituted dinitrobenzenes

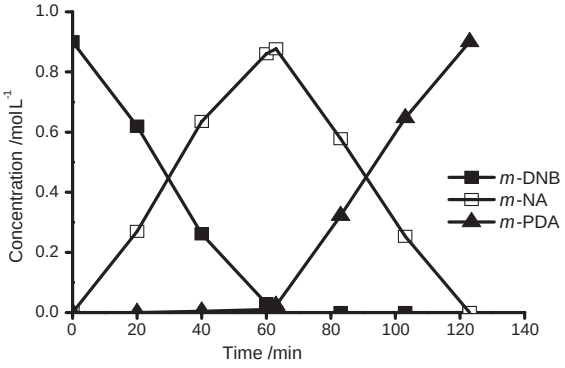


Figure 1. Product distribution as a function of time for the hydrogenation of *m*-DNB catalyzed by Ru/C (90 °C, 1.5 MPa, *m*-DNB 17 mmol, 5% Ru/C 0.1 g, CH_3OH 20 mL).

Table 1. Selective partial hydrogenation of various dinitrobenzenes to corresponding nitroanilines catalyzed by 5% Ru/C[a]

Entry	Substrate	Product	T/°C	P/MPa	Conversion/%[b]	Selectivity/%[c]
1	*m*-Dinitrobenzene	*m*-Nitroaniline	90	1.5	100	99
2	*o*-Dinitrobenzene	*o*-Nitroaniline	90	1.5	100	95
3	*p*-Dinitrobenzene	*p*-Nitroaniline	90	1.5	99	99
4	2-Methyl-1,3-dinitrobenzene	2-Methyl-3-nitroaniline	90	1.5	100	92
5	1-Methyl-2,4-dinitrobenzene	2-Methyl-5-nitroaniline 4-Methyl-3-nitroaniline	90	1.5	98	98[d] (77[e] / 21[e])
6	1,4-Dimethyl-2,5-dinitrobenzene	2,5-Dimethyl-4-nitroaniline	90	1.5	95	100
7	2,4-Dinitrophenol	2-Hydroxy-5-nitroaniline	90	1.5	100	100
8	2,4-Dinitrobenzenamine	2-Amino-4-nitroaniline 4-Amino-2-nitroaniline	90	1.5	100	99[d] (81[e] / 18[e])
9	1-Methoxy-2,4-dinitrobenzene	2-Methoxy-5-nitroaniline	90	1.5	98	96
10	3,5-Dinitrobenzoic acid	3-Amino-5-nitrobenzoic acid	50	1.0	100	97
11	2-Hydroxy-3,5-dinitrobenzoic acid	3-Amino-2-hydroxy-5-nitrobenzoic acid	50	1.0	100	95
12	1-Fluoro-2,4-dinitrobenzene	2-Fluoro-5-nitroaniline 4-Fluoro-3-nitroaniline	50	1.0	100	97[d] (46[e] / 51[e])

[a]Reaction conditions: substrate = 17 mmol, CH_3OH = 20 mL, catalyst = 0.1 g. [b]Conversion of dinitrobenzenes. [c]Selectivity of nitroanilines. [d]Total selectivity of nitroanilines. [e]Ratio of two partially hydrogenated isomers.

can be attributed to the relatively low electron density on the benzene ring, which may facilitate the reduction of nitro groups on these substrates.

Furthermore, it is worthy to note that 2,4-dinitrobenzene derivatives might produce two isomeric partially hydrogenated products. But it was interesting that the nitro group at the ortho position of most 2,4-dinitrobenzenes with electrophobic substitutent preferred to be hydrogenated than the nitro group at the para position. For example, the single partially hydrogenated products of **7a** and **9a** were 2-hydroxy-5-nitroaniline and 2-methoxy-5-nitroaniline, respectively. Additionally, **5a** and **8a** also presented obvious regioselectivity (Table 1), the products of partially hydrogenation of **8a** were 2-amino-4-nitroaniline and 4-amino-2-nitroaniline, and the ratio was 81 to 18; for **5a**, the ratio of two isomeric products was 77 to 21. It also should be noted that there was no obvious selectivity to two isomeric products (46:51) of 1-fluoro-2,4-dinitrobenzene (**12a**), which might be attributed to the inductive effects of this special deactivating group (–F).

In summary, an operationally simple and highly efficient procedure for selective partial hydrogenation of various substituted dinitrobenzenes has been developed. This catalytic transformation using Ru/C catalyst is based on a tandem process involving the initial hydrogenation of one nitro group into an amino group to obtain nitroanilines and subsequent transfer reduction of nitroanilines. We are confident that this simple methodology will be of interest to a wide range of synthetic organic chemists since it greatly facilitates the route to acquire a number of new substituted nitroanilines from dinitroaromatics. In addition, efforts to explain the mechanism of this catalytic reaction are now in progress.

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14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

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