A Convenient, Efficient, and Environmentally Benign Method for Preparing Nitroanilines

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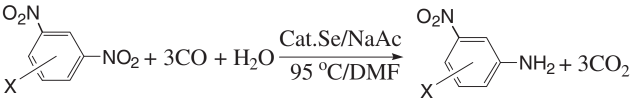
An efficient method for the catalytic monoreduction of aromatic dinitro compounds to nitroanilines is reported. In the presence of selenium catalyst, the dinitroaromatic compounds are selectively reduced by CO/H_2O to the corresponding nitroanilines under atmospheric pressure. The mono-reduction occurs in high selectivity regardless of the substitution groups on the aromatic ring without affecting other reducible functional groups.

Nitroanilines are of significant industrial importance, because they are widely used as intermediates for dyes, pharmaceuticals, and agrochemicals. The monoreduction of aromatic dinitro compounds is one of the most common methods to prepare the corresponding nitroanilines. Most often, hydrogen sulfide or variations of this reagent[1] (Zinn reduction) and iron[2] are used in industry, but large amounts of waste is produced. Recently, some homogeneous as well as heterogeneous catalytic systems in combination with different hydrogen donors have been employed for monoreduction of dinitroaromatic compounds.[3]

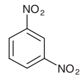
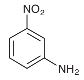
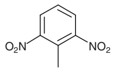
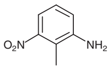
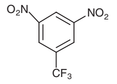
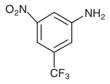
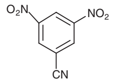
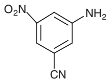
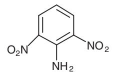
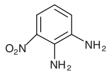
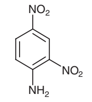
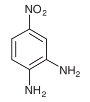
CO/H_2O as a hydrogen source for the reduction of aromatic nitro compounds to the corresponding amines is of great industrial potential, especially when a cheap catalytic system can be employed. In 1980, Sonoda[4] et al. reported the selenium-catalyzed reduction of some aromatic nitro compounds to the corresponding amines by using CO/H_2O under high pressure in the presence of triethylamine (Et_3N). But the high pressure of CO makes it difficult to apply in industry. When they extended their catalytic system to dinitro-compounds, they could not obtain the corresponding monoreduction products.[5]



(1)

Now we for the first time report the selenium-catalyzed monoreduction of dinitroaromatic compounds with carbon monoxide and water using sodium acetate (NaAc) as a base in dimethylformamide (DMF) under atmospheric pressure to give the corresponding nitroanilines (Eq 1). Besides the advantages of efficiency and convenience, the catalytic system possesses the character of phase transfer catalysis: namely, this system can be used for homogeneous catalytic reduction of dinitrobenzenes, using CO/H_2O as the reducing agent, and exhibits high conversion and selectivity as well as excellent catalyst stability. After the reaction, the catalyst and base can be easily filtered and reused just like heterogeneous catalysts. Therefore, the catalytic system possesses the advantages of both homogeneous and heterogeneous catalysts.

Table 1. The selenium-catalyzed monoreduction of dinitrobenzene derivatives to the corresponding nitroanilines[a]

Run	Substrate	Product	Reaction Time/min	Con.[c] /%	Sel.[d] /%
1			65	100	87.7
2[b]			55	100	96.4
3			60	100	78.4
4			325	50	84
5			120	100	92
6			100	100	79.0
7			140	100	83.7

[a]Reaction conditions: substrate, 10 mmol; selenium, 0.4 mmol; DMF, 40 mL; H_2O, 2 mL; NaAc, 5 mmol; CO, bubble; 95 °C. [b]DMF, 60 mL. [c]Conversion. [d]Selectivity.

m-Dinitrobenzene and five substituted dinitrobenenes were investigated and the results are summarized in Table 1. Although the reaction was complete under atmospheric pressure, all *m*-dinitrobenzene derivatives examined can be reduced to the corresponding nitroanilines with good selectivities and no ureas were detected. However, *o*- and *p*-dinitrobenzenes, in which the two nitro groups resonate with each other, cannot be reduced under our conditions. This indicates that the electron deficiency of the nitro groups prevents the reduction, as can be assumed from the fact that the reduction of the 1,3-dinitro-5-trifluoromethylbenzene is slow (Run 4). Perhaps because of the *ortho*-effect, more hindered nitro group was selectively reduced (Run 7). In addition to the mono reduction products, small amounts of diamines were also produced. The syntheses of the diamines[5] and arylureas[6] under high pressure condition have been reported previously. In particular, *o*-aminonitrobenzene prefers the formation of benzimidazolon derivatives.[7] In contrast, the carbonylation was difficult and the reduction of *m*-nitroaniline was slow[8] under our conditions, so the selectivity of amines was high and the reduction of *m*-dinitrobenzene derivatives stopped at the monoreduction stage. Although the reaction of nitriles with $Se/CO/H_2O$ in the presence of Et_3N is known to provide the corresponding selenoamides,[9] such conversion was not observed

Table 2. The influence of solvents and bases on the reduction of *m*-dinitrobenzene[a]

Run	Solvent	Base	Reaction Time[e]/min	Yield[f] /%
1	DMF	NaAc	65	87.7
2	DMSO	NaAc	120	73.9
3	1,4-Dioxane	NaAc	No reaction	–
4	Toluene	NaAc	No reaction	–
5[b]	1,2-Diethoxy-ethane	NaAc	No reaction	–
6[c]	DMF	NaAc	80	90.6
7[c]	DMF	Et_3N	300	56.5
8[c]	DMF	Na_2CO_3	240	71.7
9[c]	DMF	DBU[d]	90	55.0
10[c]	DMF	NaOH	210	60.1
11[c]	DMF	–	540	95.0

[a] Reaction conditions: dinitrobenzene 10 mmol, base 5 mmol, solvent 40 mL, H_2O 2 mL, CO bubble, 95 °C. [b] 92 °C. [c] 85 °C. [d] 1,8-Diazabicyclo[5.4.0]undec-7-ene. [e] The time when the conversion of *m*-dinitrobenzene reached to 100%. [f] Isolated yield is based on *m*-dinitrobenzene.

in our reactions. The sensitive functional groups, e.g., cyano, cannot be reduced at all (Table 1, Run 5).

Why is the nitro groups reduced so well by CO/H_2O under the mild conditions ? We think the selection of solvent is of great importance on this reduction. The effects of solvents on the reaction are shown in Table 2. As can be seen from these data, polar aprotic solvents are essential. In the experiments, with the blowing of carbon monoxide, we can see that selenium can dissolve quickly in the polar aprotic solvents (such as DMF) even in the absence of bases. This process is impossible in less polar solvents. In the presence of Et_3N, the process is slow in the nonpolar solvents. This indicates that the polar aprotic solvents are favorable for the formation of carbonyl selenide and promote the nucleophilic attack of water to generate selane (H_2Se), which (or its anion, i.e., HSe^-) is regarded as the active intermediate in $Se/CO/H_2O$ reducing system.[4]

Table 3. The recycling of catalyst for the mono-reduction of *m*-dinitrobenzen[a]

Catalyst	Reaction Time /min	Conversion /%	Selectivity[b] /%
Fresh	65	100	87.7
Recycle 1	70	100	90.6
Recycle 2	65	100	88.4

[a]Reaction conditions: *m*-dinitrobenzene, 10 mmol; selenium, 0.4 mmol; DMF, 40 mL; H_2O, 2 mL; NaAc, 5 mmol; CO, bubble; 95 °C. [b]Based on *m*-nitroaniline.

The bases accelerate the reduction but they are not essential. Even without bases the reaction can proceed slowly (Table 2, Run 11). NaAc is suitable for this reduction. Organic bases, which are favorable for carbonylation and reduction under high pressure, are not effective for this reaction under atmospheric pressure (Table 2, Runs 7 and 9).

At the end of catalytic reduction of *m*-dinitrobenzene, the catalyst was precipitated and recovered. As shown in Table 3, the catalytic activity of the recovered catalysts was practically the same as that of the fresh catalyst, indicating the excellent stability of the catalyst.

A typical reaction procedure is described as follows:

The reduction was carried out in a 100-mL-three-necked flask fitted with a gas inlet tube, a condensator and a magnetic stirring bar. Substrates, water, selenium powder, anhydrous NaAc, and the solvent were placed in the three-necked flask. CO was introduced into the flask and the mixture was heated to the given temperature. When the reaction was complete, the mixture was cooled to room temperature and CO bubbling was stopped. Then air was introduced into the reaction mixture to precipitate selenium. After filtration of selenium, evaporation of the solvent and purification by column chromatography on silica gel, led to the corresponding nitroanilines. The structures of the products were assigned by a comparison of their mp., ^1H and ^{13}C NMR spectra with those of the authentic compounds. The recovered selenium by filtration can be reused.

In summary, we have developed the selenium-catalyzed monoreduction process of dinitroaromatic compounds with CO/H_2O using sodium acetate as a base under atmospheric pressure, which gives the corresponding nitroanilines. During the reduction, other reducible functional groups such as cyano group remain unchanged.

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8 Reaction conditions: *m*-nitroaniline, 10 mmol; selenium, 0.4 mmol; DMF, 40 mL; H_2O, 2 mL; NaAc, 5 mmol; CO, bubble; 95 °C, 5 h. The conversion of *m*-nitroaniline is 53%, the selectivity of benzene-1,3-diamine is 100%.

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