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Selective formation of nitroanilines by selenium-catalyzed monoreduction of dinitrobenzenes with CO/H_2O

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ABSTRACT

Nitroanilines are synthesized via selenium-catalyzed monoreduction of dinitrobenzenes with CO/H_2O. The monoreduction occurs in high selectivity regardless of other reducible functionalities on the aromatic ring. This catalytic reaction is important from both synthetic and industrial points of view, because the reaction can be carried out with high yields of desired nitroanilines not only under high pressure but also under atmospheric pressure. There exists a phase-transfer process of the selenium catalyst in the reaction, which makes the catalyst easily separated from the reaction system by simple phase separation.

1. Introduction

Monoreduction of aromatic dinitro-compounds to prepare the corresponding nitroanilines is of immense industrial importance, because nitroanilines are widely used as intermediates for dyes, pharmaceuticals and agrochemicals. Generally, hydrogen sulfide or variations of this reagent [1] (Zinn reduction) and iron [2] are used in industry, but large amounts of waste are produced.

Applying catalytic methods in the selective reduction of dinitroaromatic compounds is interesting and useful in the viewpoint of science and industry, and it is the demand of green chemistry. Some homogeneous as well as heterogeneous catalytic systems in combination with different hydrogen donors have been employed for selective reduction of dinitroaromatic compounds [3–8]. CO/H_2O as a hydrogen source for the reduction of aromatic nitro compounds to prepare the corresponding amines is of great industrial potential and is widely researched [9–14], especially when a cheap catalytic system can be employed. In 1980, Sonoda and coworkers [15] firstly reported selenium-catalyzed reduction of some aromatic nitro compounds affording the corresponding amines by using CO/H_2O under high pressure in the presence of triethylamine (Et_3N). When they extended their catalytic system to dinitro-compounds, they could not obtain the corresponding monoreduction products [16].

We reported selenium-catalyzed reduction of aromatic nitro compounds to give the corresponding amine by using CO/H_2O under atmospheric pressure [17]. Recently, our studies on selenium-catalyzed reductions have been extended to the synthesis of nitroanilines [18,19].

In this work, we report the synthesis of nitroanilines via selenium-catalyzed monoreduction of dinitrobenzenes with carbon monoxide and water. This reaction can be carried out with high selectivity of desired nitroanilines not only under high pressure but also under atmospheric pressure.

2. Experimental

Reagent: Carbon monoxide (99.9%) was dried with molecular sieve 5A. Elemental selenium (99.999%), substrates, bases and solvents were used as purchased without further purification. Melting points were determined on a Taike X-4 apparatus (Beijing, China) and were uncorrected. ^{13}C and ^{1}H NMR spectra were recorded on a Bruker DRX 400 spectrometer with $CDCl_3$ as solvent and Me_4Si as an internal standard.

Typical procedures for the synthesis of nitroanilines are described as follows.

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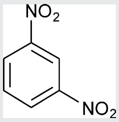
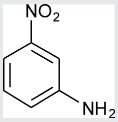
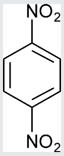
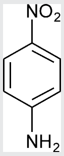
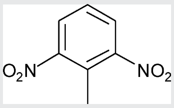
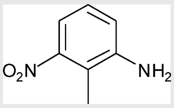
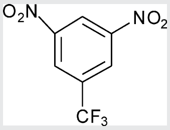
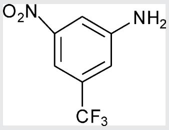
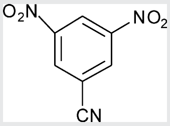
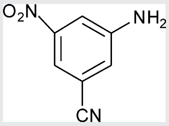
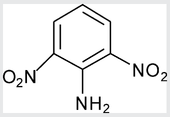
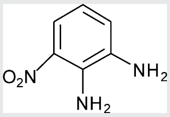
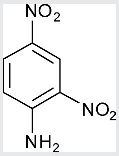
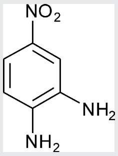
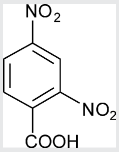
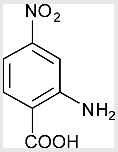
Table 1
Selenium-catalyzed monoreduction of dinitrobenzene derivatives affording the corresponding nitroanilines under high pressure.

Entry	Substrate	Product	m.p. (°C)		Conversion (%)	Yield (%)[a]
			Found	Literature		
1[b]			112–114	114 [26]	100	95.7
2[c]			112–114	114 [26]	100	83.3
3[b]			144–147	148 [26]	100	78.3
4[d]			87–89	92 [26]	100	90.8
5[b]			80–82	80–81.5 [26]	100	79.6
6[b]			167–169	167.5–169 [27]	94.8	52.8
7[b]			155–156	158–159 [28]	100	59.9
8[b]			204	204 [29]	100	46.1
9[e]			210–213	211–213 [30]	100	59.3

[a] Isolated yield is based on substrate.

[b] Reaction conditions: Substrate, 10 mmol; selenium, 0.4 mmol; THF, 15 mL; H_2O, 0.2 mol; P(CO) = 1 MPa; 160 °C; t = 3 h.

[c] Substrate, 5 mmol; selenium, 0.2 mmol; THF, 30 mL; H_2O, 0.1 mol; NaAc, 5 mmol; P(CO) = 0.5 MPa; 160 °C; t = 2 h.

[d] The same conditions as b but t = 6 h.

[e] The same conditions as b but with acetone (15 mL) instead of THF.

2.1. High pressure procedure

The reduction was carried out in a 100 mL stainless steel autoclave with a magnetic stirring bar. Substrate, water, selenium powder, anhydrous sodium acetate (NaAc) and solvent tetrahydrofuran (THF) were placed in the autoclave. The autoclave was sealed and flushed 3 times with 2 MPa of CO, and then charged with needed pressure of CO. After that, the reactor was placed in an oil bath preheated to 160 °C for 3 h with vigorous stirring. When the reaction was complete, the reactor was cooled to room temperature and depressurized. Then air was introduced into the reaction mixture to precipitate selenium. After filtration of selenium and evaporation of the solvent, the product was collected and purified by column chromatography on silica gel using Et_2O–AcOEt (5:1–5:2) as the eluent.

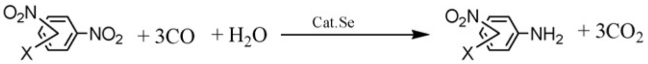
2.2. Atmospheric pressure procedure

The reduction was carried out in a 100 mL three-necked flask fitted with a gas inlet tube, a condenser and a magnetic stirring bar. Substrates, water, selenium powder, anhydrous sodium acetate (NaAc), and the solvent were placed in the three-necked flask. It was then placed in an oil bath preheated to the given temperature and CO (20 mL/min) was bubbled through the reaction mixture with vigorous stirring. The reaction was monitored by TLC determination. When the reaction was complete, the mixture was cooled to room temperature and CO bubbling was stopped. The resultant mixture was exposed to air and further stirred for about one hour to precipitate selenium. After filtration of selenium, the mixture was distilled under reduced pressure. The crude product was purified as described above for the high pressure procedure.

3. Results and discussion

3.1. *Selective reduction of dinitrobenzene under high pressure*

Monoreduction of dinitrobenzenes and six substituted dinitrobenenes was investigated and the results are summarized in Table 1. When the initial CO pressure was 1 MPa, most dinitrobenzene derivatives were reduced affording the corresponding nitroanilines with yields from moderate to good. Unlike the monoreduction by sulfide reagents and stannous chloride, all the hindered nitro groups were selectively reduced (entries 8 and 9). It seems that the electronical effect of substituted groups is not obvious. In addition to products, small amounts of diamines and arylureas were produced, which made the margin between the conversions of dinitroaromitic compounds and the yields of the corresponding nitroanilines. The synthesis of the diamines [16] and arylureas [20–22] in similar conditions was reported previously. In particular *o*-amino dinitrobenzenes prefer producing benzimidazolons [23], which is consistent with the relatively low yields of monoreduction from 2, 6-dinitro-aniline and 2, 4-dinitro-aniline (entries 7 and 8). However, the dilution of reactant is disadvantageous to the synthesis of arylureas, which was favorable for the reduction. That may be the reason why *m*-dinitrobenzene can be reduced to *m*-nitroaniline in a high yield (entry 1). Although with Et_3N as co-reagent, the nitriles can react with Se/CO/H_2O to give selenoamides [24,25], this conversion did not occur under our conditions. The sensitive functional groups, e.g. cyano, carboxyl and trifluoro methyl, remained unchanged during the reduction (Entries 5, 6 and 9).



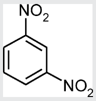
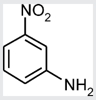
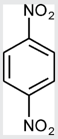
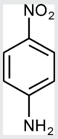
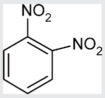
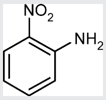
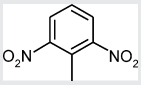
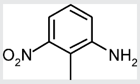
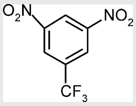
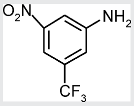
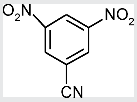
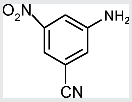
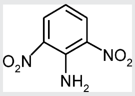
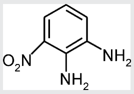
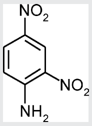
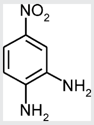
Scheme 1.

3.2. *Monoreduction of dinitrobenzenes under atmospheric-pressure*

The monoreduction of dinitrobenzenes can be carried out with high yields under high pressure, but the high pressure of CO makes it difficult to apply in industry. We have found that the selenium-catalyzed monoreduction of aromatic dinitro compounds with CO/H_2O gives the corresponding nitroanilies in the solvent of dimethylformamide (DMF) under atmospheric pressure (Scheme 1).

Dinitrobenzenes and five substituted dinitrobenenes were investigated and the results are summarized in Table 2. Although these reactions were carried out under atmospheric pressure, all *m*-dinitrobenzene derivatives examined can be reduced to the corresponding nitroanilines in good selectivities and no ureas were detected. However, *o*- and *p*-dinitrobenzenes, in which the two nitro groups resonance with each other, cannot be reduced under atmospheric pressure, owing to the electron-withdrawing character of nitro group [17]. This indicated the electron deficiency of the nitro groups prevents the reduction, as can be assumed from the fact that the reduction of 1, 3-dinitro-5-trifluoromethyl-benzene was slow (entry 5). Perhaps because of the *ortho*-effect more hindered nitro groups were selectively reduced (entry 8), which is the

Table 2
Selenium-catalyzed monoreduction of dinitrobenzene derivatives affording the corresponding nitroanilines under atmospheric pressure.

Entry	Substrate	Product	Reaction time (min)	Conversation (%)	Selectivity (%)
1			65	100	87.7
2			120	0	–
3			120	0	–
4			60	100	78.4
5			325	50	84
6			120	100	92
7			100	100	79.0
8			140	100	83.7

Reaction conditions: substrate, 10 mmol; selenium, 0.4 mmol; DMF, 40 mL; H_2O, 2 mL; NaAc, 5 mmol; 95 °C.

Table 3
The effect of solvents and bases on the reduction of *m*-dinitrobenzene under atmospheric pressure[a].

Entry	Solvent	Dielectric constant	Base	Amount of base (mmol)	Reaction time[b] (min)	Yield[c] (%)
1	DMF	36.71^{25} [32]	NaAc	5	65	87.7
2	DMSO	48.9^{20} [32]	NaAc	5	120	73.9
3	Acetonitrile	37.5^{20} [32]	NaAc	5	240	0
4[d]	THF	7.58^{25} [32]	NaAc	5	240	0
5	Toluene	2.24^{20} [32]	NaAc	5	240	0
6[e]	1,2-Diethoxy-ethane	5.10^{25} [32]	NaAc	5	240	0
7[f]	DMF	36.71^{25} [32]	NaAc	5	80	90.6
8[f]	DMF	36.71^{25} [32]	Et_3N	5	300	56.5
9[f]	DMF	36.71^{25} [32]	Na_2CO_3	5	240	71.7
10[f]	DMF	36.71^{25} [32]	DBU[g]	5	90	55.0
11[f]	DMF	36.71^{25} [32]	NaOH	5	210	60.1
12[f]	DMF	36.71^{25} [32]	–	0	540	95.0
13[f]	DMF	36.71^{25} [32]	NaAc	2.5	85	90.6

[a] Reaction conditions: dinitrobenzene 10 mmol, base 5 mmol, solvent 40 mL, H_2O 2 mL, 95 °C.

[b] The time when the conversion of *m*-dinitrobenzene reached 100%.

[c] Isolated yield is based on *m*-dinitrobenzene.

[d] 60 °C.

[e] 92 °C.

[f] 85 °C.

[g] 1,8-Diazabicyclo[5.4.0]undec-7-ene.

same as the results of the reduction under high pressure (entries 8 and 9 in Table 1). In addition to the monoreduction products, small amounts of diamines were also produced. The carbonylation was difficult and the reduction of *m*-nitroaniline was slow [31] in our conditions, so the selectivities for nitro anilines were high and the reduction of *m*-dinitrobenzene derivatives stopped at the monoreduction stage. Just as those in the reduction under high pressure, the sensitive functional groups (e.g., cyano) were not reduced at all in the reduction under atmospheric pressure (entry 6).

3.3. The effect of solvents and bases

For the selenium-catalyzed monoreduction of dinitrobenezenes under atmospheric pressure, the solvents play an important role in the process of the reaction pressure change from high pressure to atmospheric pressure. The effects of solvents on the reduction under atmospheric pressure are shown in Table 3. As can be seen from these data, polar aprotic solvents were essential. In the experiments, with the blowing of carbon monoxide, selenium can dissolve quickly in the polar aprotic solvents (such as DMF) even in the absence of bases. This process is impossible in the less polar solvents. This indicates that the polar aprotic solvents are favorable for the formation of carbonyl selenide (SeCO) and promote the nucleophilic attack of water to generate selane (H_2Se or its anion, i.e., HSe^-), which is regarded as the active intermediate in the Se/CO/H_2O reducing system [15]. Not all polar aprotic solvents were, however, suitable for the atmospheric reaction, e.g., acetonitrile (entry 3).

The bases accelerated the reduction but were not essential. With the decrease in the amount of base, the rate of reaction decreased and yields increased (entries 1, 12 and 13). Even without bases the reaction proceeded slowly (entry 12). NaAc was suitable for the reduction. Organic bases, which were favorable for carbonylation under high pressure, were not effective for the reduction under atmospheric pressure (entries 8 and 10).

3.4. The effect of the concentrations of substrate and water

The effect of the concentrations of substrate and water on the *m*-dinitrobenzene reduction under atmospheric pressure is shown in Table 4. The rate and selectivity of the reduction decreased when the concentration of substrate was increased (entries 1–4).

With the increase in water, the rate and selectivity of the reduction decreased (entries 2, 7 and 8). In contrast, with the increase in DMF, the rate and selectivity of the reaction increased (entries 2, 5 and 6). Water is not only a reactant but also a solvent. These indicate that the increase in the ratio of water to DMF destroys the aprotic character of the solvent. So the formation of active intermediates is difficult and the rate of reduction decreases.

3.5. The phase-transfer function of selenium-catalyzed system

For homogeneous catalytic systems, separation and reuse of catalyst are difficult. However, it is interesting that the selenium

Table 4
The effect of substrate and water on the selenium-catalyzed monoreduction of *m*-dinitrobenzene to *m*-nitroaniline under atmospheric pressure[a].

Entry	Substrate (mmol)	DMF (mL)	Water (mL)	Reaction time (min)	Conversion (%)	Yield[b] (%)
1	5	40	2	30	100	97.4
2	10	40	2	65	100	87.7
3	15	40	2	205	100	83.3
4	20	40	2	360	100	81.1
5	10	20	2	360	100	36.2
6	10	60	2	55	100	96.4
7	10	40	4	85	100	83.3
8	10	40	8	150	100	73.9

[a] Reaction conditions: selenium 0.4 mmol, NaAc 5 mmol, 95 °C.

[b] Isolated yield is based on *m*-dinitrobenzene.

Table 5
Recycling of catalyst for the mono-reduction of *m*-dinitrobenzene[a].

Catalyst	Reaction time (min)	Conversation (%)	Yield[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; 95 °C.

[b] Isolated yield is based on *m*-nitroaniline.

catalyst can be recycled for use. At the end of catalytic reduction of dinitrobenzene, carbon monoxide bubbling was stopped. Then air was introduced into the flask and the catalyst was precipitated and recovered. The catalytic activities of the recovered catalysts were practically the same as those of the fresh catalyst, indicating the excellent stability of the catalyst (Table 5). Before the reaction, the selenium catalyst is in the solid state in the selenium-catalyzed system, which is different in phase from the reagents. During the reaction process, selenium reacts with carbon monoxide to form SeCO, which can dissolve in the solvent to form a homogeneous catalytic system. In the solvent, SeCO reacts with water to form selane (or its anions), which reduces the dinitrobenzenes to nitroanilines and is oxidized to selenium. Thus, there exists a phase transfer phenomenon of catalyst in this catalytic reaction system. Namely, the reaction system changes from the heterogeneous system to the homogeneous system and return to the heterogeneous system. The character of phase transfer enables toxic selenium catalysts to be easily separated from the product and reused by simple phase separation.

4. Conclusions

In summary, we have developed the selenium-catalyzed monoreduction process of dinitro aromatic compounds with CO/H_2O using sodium acetate as a base affording the corresponding nitroanilines. During the reduction, other reducible functional groups, such as cyano group, remain unchanged. This would represent a very convenient reduction protocol to give nitroanilines.

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