Communication

Preparation of Aromatic Amines by Reduction of Aromatic Nitro Compounds with Metallic Tellurium in Near-Critical Water

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Aromatic amines were prepared in good yields by a novel reduction of aromatic nitro compounds with tellurium metal in near-critical water at 275 ℃.

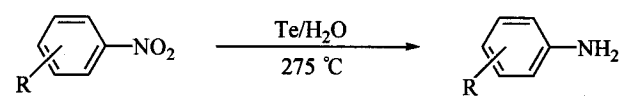
Keywords aromatic amine, reduction, aromatic nitro compound, metallic tellurium, near-critical water (NCW)

Aromatic amines, widely used as important intermediates in the synthesis of dyes, antioxidants, photographic, pharmaceutical and agricultural chemicals, can be prepared by reduction of the corresponding aromatic nitro compounds using catalytic hydrogenation,[1] hydrazine, $Ru_3(CO)_{12}$, $TiCl_4$-dialkyl telluride, active metal, metal hydride complexes and sulfides, respectively.[2-9] The most classic and practical method is the reduction of nitro compounds with zinc, tin, or iron in the presence of an acid.[10,11] However, the reduction of aromatic nitro compounds often yields a mixture of products and most of chemical methods are lack of the chemoselectivity over other functional groups.[12-14] In addition, the reactions are generally carried out in organic solvents or in the presence of acids, which pose waste handling problems.

Organic reactions carried out in water have received much more attention in last decade.[15-18] Unfortunately most of organic compounds are poorly soluble in water at ambient temperature. Nonetheless, the unique properties of water near its critical point (T_c = 374 ℃, $p_c = 2.18 \times 10^7$ Pa) have promoted researchers to use it instead of organic solvents or ambient temperature water in organic synthesis.[19-21] Although most of supercritical water research has focused on the total oxidation of organic compounds and geochemical modeling,[22-26] there are increasing numbers of papers which suggest that near-critical water (NCW) (250—325 ℃) can be an excellent solvent for organic reactions because reactions in near-critical water offer many advantages over those in traditional organic solvents. For example, it is environmentally benign and separation of products from reaction mixture is simplified.[27-31]

Recently, Poliakoff *et al.*[32] reported the selective reduction of nitroarenes to anilines with metallic zinc in near-critical water (250 ℃). To our knowledge, so far there is no report on the reduction of aromatic nitro compounds to aromatic amines with tellurium metal in water. Here we wish to report a novel reduction of aromatic nitro compounds by using metallic tellurium powder in near-critical water (275 ℃), in which the corresponding aromatic amines were abtained in good yields.

Scheme 1



General procedure for the reduction of aromatic nitro compounds with metallic tellurium in near-critical water

Aromatic nitro compound (1.00 mmol) and metallic tellurium powder (100—200 mesh, 383 mg, 3.00 mmol) were added to a high temperature and pressure stainless steel reactor charged with tap water (10 mL) under nitrogen atmosphere. The reactor was heated at 275 ℃ for 5 h on oven. After cooling, ethyl ether (2 × 10 mL) was added to extract the products. After the organic layer was dried with anhydrous sodium sulfate, the solvent was evaporated under reduced pressure. The product was purified by flash chromatography to yield aromatic amine.

Our initial studies were directed toward exploring the reaction conditions for the reduction of aromatic nitro compounds with metallic tellurium powder in hot water. The results are summarized in Table 1. Nitrobenzene was chosen as the model compound for this investigation.

As can be seen from Table 1, the reaction temperature plays a very important role in the reduction of nitrobenzene with metallic tellurium in water. It is evident that the reduction of nitrobenzene was not completed at $T \leqslant 225$ ℃ without any additive (Entry 1, Table 1). When the reaction tempera-

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Table 1 Optimization of reaction conditions for the reduction of nitrobenzene[a]

Entry	Te:Nitrobenzene	Temperature (℃)	Time (h)	Yield[b] (%)
1	3:1	225	5	43
2	3:1	250	5	71
3	3:1	275	5	78
4	3:1	300	5	77
5	1:1	275	5	38
6	2:1	275	5	69
7	4:1	275	5	78
8	3:1	275	1	28
9	3:1	275	3	64
10	3:1	275	7	76

[a] Reaction conditions: nitrobenzene (1.00 mmol), tap water (10 mL) in a high T/p batch reactor system. [b] Isolated yields.

ture is at 250 ℃, the yield of aniline is improved significantly. The effect of the ratio of tellurium to nitrobenzene was also examined. The results show that when the ratio of tellurium to nitrobenzene is less than 2:1, the reduction is not completed (Entries 5 and 6, Table 1), and while the ratio equals or is more than 3:1, satisfactory results are achieved (Entries 4 and 7, Table 1). We also investigated the effect of reaction time. The experimental data indicate that the reaction is not completed when reaction time is less than 3 h (Entries 8 and 9, Table 1). However, no increase of yield was observed when reaction time was prolonged (Entries 10, Table 1). The optimized conditions for the reduction of nitrobenzene with tellurium metal in water were found to be Te (3 eq.), nitrobenzene (1 eq.), H_2O (10 mL) at 275 ℃ for 5 h.

Table 2 Reduction of aromatic nitro compounds with tellurium metal in NCW[a]

Entry	Aromatic nitro compound	Aromatic amine	Yield[b] (%)
1	$C_6H_5NO_2$	$C_6H_5NH_2$	78
2	p-$CH_3C_6H_4NO_2$	p-$CH_3C_6H_4NH_2$	89
3	m-$CH_3C_6H_4NO_2$	m-$CH_3C_6H_4NH_2$	90
4	m-$CH_3COC_6H_4NO_2$	m-$CH_3COC_6H_4NH_2$	76
5	p-$ClC_6H_4NO_2$	p-$ClC_6H_4NH_2$	82
6	o-$ClC_6H_4NO_2$	o-$ClC_6H_4NH_2$	71
7	m-$ClC_6H_4NO_2$	m-$ClC_6H_4NH_2$	80
8	p-$BrC_6H_4NO_2$	p-$BrC_6H_4NH_2$ $C_6H_5NH_2$	42[c] 30[c]
9	o-$IC_6H_4NO_2$	$C_6H_5NH_2$	67
10	p-$HO_2CC_6H_4NO_2$	$C_6H_5NH_2$	70
11	*trans*-$C_6H_4CH=CHNO_2$	—	0[d]
12	$C_{10}H_7NO_2$	$C_{10}H_7NH_2$	87
13	p-$CH_3CONHC_6H_4NO_2$	p-$CH_3CONHC_6H_4NH_2$	74

[a] Reaction conditions: aromatic nitro compound (1.00 mmol), metallic tellurium powder (3.00 mmol), tap water (10 mL) in a high T/p batch reactor system at 275 ℃ for 5 h. [b] Isolated yields. [c] Determined by GC and NMR analyses of the reaction mixture. [d] Starting material (2-nitrovinyl)benzene (95%) was recovered.

A variety of aromatic nitro compounds were successfully reduced to the corresponding aromatic amines with metallic tellurium powder in near-critical water (275 ℃). The results are summarized in Table 2. The data in Table 2 indicated that the electronic characteristics of a general electron-donating group (such as CH_3) or a general electron-withdrawing group (such as CH_3CO, Cl) and its location on the aromatic ring are relatively insensitive to the reaction. However, bromo or iodo group on the aromatic ring underwent reductive elimination of the Br or I in a competitive process, but chloro group could tolerate the reaction conditions and remain unchanged. The reactivity of halogen atoms on the aromatic ring is I > Br > Cl, which is consistent with the expected reactivity and Poliakoff's experimental results.[32] Carboxylic group on the aromatic ring also underwent the decarboxylation process. Futhermore, the reduction does not occur in aliphatic nitro compounds. Unfortunately, attempt to reduce *trans*-β-nitrostyrene, in which the nitro group conjugated with carbon-carbon double bond, was failed.

In conclusion, a novel, reliable and practical synthetic method for the preparation of aromatic amines has been developed, which involves the use of tellurium metal as reductive agent and aromatic nitro compounds as starting material in near-critical water (275 ℃). The method has the advantages of simple operation, good chemoselectivity and use of a cheap, nontoxic, nonflammable solvent.

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