Reduction of Aromatic Nitro Compounds Using Samarium Metal in the Presence of a Catalytic Amount of Iodine under Aqueous Media

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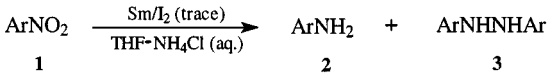
Abstract: In the presence of a catalytic amount of iodine, aromatic nitro compounds can be reduced to the corresponding primary amines and hydrazines in good yields with Sm/THF-NH_4Cl (aq.) system at room temperature. The primary amine is in the majority and the halogen, amido substituents on aromatic ring are unaffected during the reaction.

Key words: reduction, aromatic nitro compounds, samarium metal, aqueous media, aromatic amines

Samarium diiodide and organosamarium compounds have been widely employed as useful reagents in organic synthesis[1]. However, relatively few reports on the direct use of samarium metal in organic synthesis have been reported[2], because the surface of samarium metal is unactive[3]. In order to improve the reactivity of samarium, some additives, such as $HgCl_2$[4], TMSCl[5] or NH_4Cl (aq.)[6] were added for this purpose. Hou et al have reported the use of samarium metal in the presence of a catalytic amount of allyl iodide for the selective synthesis of aromatic azoxy compounds from reduction of nitroarenes[7].

Aromatic amines, widely used as intermediate for dyes, photographic, pharmaceutical and agricultural chemicals and antioxidants, can be easily prepared by reduction of aromatic nitro compounds using a variety of reductant, such as catalytic hydrogenation[8], carbon monoxide and ruthenium carbonyl[9], titanium (IV) chloride and dialkyl telluride[10], etc. The drawback of the former method is lack of chemoselectivity, while the later method require rather long reaction time, high cost and toxicity of the reagents and usually results only in poor yields. Recently, there are some reagents, such as diethyl chlorophosphite[11], N, N-dimethyl hydrazine/ferric chloride (cat.)[12], nickel-stabilized zirconia[13], hydrazine hydrate/iron(III) oxide-MgO(cat.)[14] and indium metal[15], reported for the modification of this transformation. We report herein the reduction of aromatic nitro compounds using samarium metal in the presence of a catalytic amount of iodine under aqueous media at room temperature.

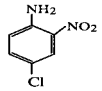
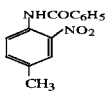


Scheme

The results of reduction of aromatic nitro compounds using samarium are summarized in **Table**. We found that the reduction of aromatic nitro compounds proceeded smoothly in the presence of a catalytic amount of iodine with metallic samarium under aqueous NH_4Cl-THF condition at room temperature. The reactions are completed within 6 hours, and give the corresponding primary amine and hydrazine in moderate to good yields. The amine is in the majority. In the course of this process, substituents such as chloro, bromo, iodo, methyl, methoxy, or amide groups are not affected. The experimental results indicated no dehalogenation, demethylation or hydrolysis was observed during the reaction.

Interestingly, addition of trace amount of iodine not only accelerates the reduction of aromatic nitro compounds, but also increases the yields of products. However, aromatic amine as a major product in this reaction is different from aromatic azoxy compounds as a major product in Hou's results[7]. This difference is not full clearly till now and the study concerning about this is in progress in our laboratory.

Table Reduction of aromatic nitro compounds using samarium metal in the presence of a catalytic amount of iodine under aqueous media

Entry	Substrate	Time (h)	Yield (%) [a]	
			2	3
a	$C_6H_5NO_2$	4	56	20
b	4-$BrC_6H_4NO_2$	4	70	18
c	4-$ClC_6H_4NO_2$	4	65	--
d	3-$BrC_6H_4NO_2$	4	63	--
e	3-$IC_6H_4NO_2$	4	68	--
f	4-$CH_3C_6H_4NO_2$	5	60	--
g	3-$CH_3OC_6H_4NO_2$	5	62	--
h		6	74	14
i		6	65	16

a. Isolated yields

In conclusion, we have demonstrated that Sm-I_2 (trace)/ THF-NH_4Cl (aq.) system can be used for the selective reduction of aromatic nitro compounds to the corresponding aromatic amines. The notable advantages of this reaction are its simplicity, mild reaction conditions and good yields. It provides a new way for using metallic samarium in organic synthesis.

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References and Notes

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(16) Typical procedure: Under an inert atmosphere of nitrogen, metallic samarium powder (0.6 g, 4.0 mmol) and aromatic nitro compound (1.0 mmol) were placed in a round-bottomed flask. Then THF (5 mL), a small grain of iodine and NH_4Cl (aq., 0.5 mL) were added successively to it. The reaction mixture was stirred for the time indicated in **Table** at room temperature. The reaction was then quenched by the addition of HCl (1 mol/L, 2 mL). The mixture was extracted with ether (25 mL x 2). The combined organic layer was washed with brine, dried over magnesium sulfate, and concentrated. The product was isolated by preparative TLC on silica gel eluting with cyclohexane-ethyl acetate (3:1).

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