

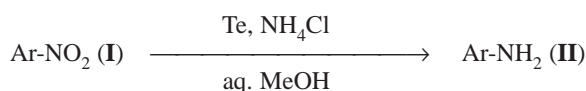
Tellurium mediated reduction of aromatic nitro groups[†]

Rahat H. Khan*

Indian Institute of Petroleum, Dehradun – 248 005, India

Treatment of a wide range of aromatic nitro compounds with tellurium powder in aqueous methanolic ammonium chloride results in selective reduction of the nitro groups; ester, nitrile, amide and halide substituents are unaffected.

Although a large number of methods for the reduction of aromatic nitro compounds have been developed,¹ many of these are incompatible with other functional groups in the molecule. For example, the selective reduction of nitro groups in the presence of carbonyl groups, nitriles, halides and alkenes is often difficult, and in such cases catalytic hydrogenation, which is often the method of choice for nitro reduction, is inappropriate. Thus, hydrogenation of 4-chloro-3-nitroacetophenone over Pd/C results in hydrogenolysis of the halide, and reduction of the ketone as well as nitro groups.² Consequently new methods for the selective reduction of nitro groups continue to be developed.³ We now report a mild new method for the reduction of aromatic and heteroaromatic nitro groups using tellurium metal powder (Scheme 1).



Scheme 1

Development of new synthetic reactions utilizing characteristics of tellurium and its compounds has recently attracted much attention.⁴ As part of a wider study on the use of tellurium metal and its compounds in organic synthesis,⁵ we found that the reduction of aromatic nitro compounds proceeded readily on heating the substrate with the tellurium powder in aqueous methanolic ammonium chloride. The reactions are extremely easy to carry out, are typically complete within 2–5 h, and give the corresponding aniline in good to excellent yield (Table 1). The reaction conditions are compatible with halogen substituents (Cl, Br, I; entries 1–3), carbonyl groups (acid, ester, amide; entries 4, 6, 7) and nitrile (entry 5), and the reduction is not affected by the presence of

sulfur containing substituent (entry 8). In 6-nitroquinoline and 5-nitroisoquinoline, the group is reduced before the heterocyclic ring (entries 10, 11). In a typical procedure, to a solution of the nitro compounds (5 mmol) in methanol (50 ml) was added saturated ammonium chloride solution (5 ml, 75 mmol) tellurium powder (3.0 g, 23 mmol). The mixture was stirred under reflux. When the reaction appeared complete as monitored by TLC (typically 2–5 h), the cooled reaction mixture was diluted with water (100 ml) and filtered through Celite. The aqueous filtrate was adjusted to pH~9 with NaOH (4M) and extracted with dichloromethane/ethyl acetate (3 × 50 ml). The combined organic layers were dried (Na₂SO₄). Removal of solvent and chromatography on silica gel gave the anticipated products.

In conclusion, the use of tellurium metal powder for the selective reduction of aromatic nitro compounds is simple, occurs under mild conditions and in high yield. Therefore, this should prove a valuable addition to synthetic methodology.

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Table 1 Reduction of aromatic and heteroaromatic nitro compounds using tellurium metal powder in aqueous methanolic ammonium chloride

Entry	Substrate I	Time/ (h)	Product II	Yield ^a (%)	(b.p.) m.p. (°C)	
					Found	Reported
1	1-Chloro-4-nitrobenzene	3	4-Chloroaniline	95	68–71	71 ⁶
2	4-Bromo-2-nitrotoluene	5	4-Bromo-o-toluidine	75	55–58	59 ⁶
3	Iodo-2-nitrobenzene	3	2-Iodoaniline	62	54–57	60–61 ⁶
4	3-Nitrobenzoic acid	2	3-Aminobenzoic acid	90	172–173	174 ⁶
5	3-Nitrobenzotrile	2	3-Aminobenzotrile	86	50–52	53–54 ⁶
6	Ethyl 4-nitrobenzote	3	Ethyl 4-aminobenzote	95	88–89	88–90 ⁶
7	4-Nitroacetanilide	4	4-Aminoacetanilide	85	161–162	162–63 ⁶
8	Methyl 4-nitrophenyl sulfide	5	4-(Methylthio) aniline	94	(260–270)	(272–273) ⁶
9	4-Nitrophenetole	4	4-Aminophenetidine	82	(235–255)	(254) ⁶
10	6-Nitroquinoline	3	6-Aminoquinoline	86	112–113	114 ⁶
11	5-Nitroisoquinoline	5	5-Aminoisoquinoline	80	125–126	128 ⁶
12	1,3-Dimethyl-2-nitro-5- t-butylbenzene	5	2,6-Dimethyl-4-t-butylaniline	81	(240–260)	(89–91/1 torr) ⁷

^aThe product anilines are known compounds whose spectral data (IR 1H NMR) agreed closely with literature values.^{7,8}

* To receive any correspondence. E-mail: rhkhan@iip.res.in

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

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