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Synthesis of *N*-Arylhydroxylamines by Tellurium-Catalyzed Reduction of Aromatic Nitro Compounds

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p-Substituted nitrobenzenes were readily reduced with sodium borohydride and a catalytic amount of tellurium to give the corresponding hydroxylamines in good yields.

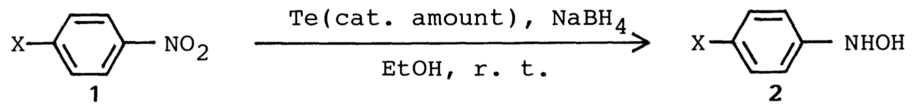
In recent years, the utility of new reducing reagents containing tellurium element has been recognized in organic synthesis[1] and it has been shown that these reductive species (H_2Te, NaTeH, PhTeH, and Na_2Te) can effect the reduction of aromatic nitro compounds to azoxy,[2] azo,[3] and amino compounds.[4] We have now found that the combination of sodium borohydride and a catalytic amount of tellurium is very effective for the partial reduction of *p*-substituted nitrobenzenes (**1**) to *N*-arylhydroxylamines (**2**). In this letter, we wish to describe a mild and efficient synthesis of *N*-arylhydroxylamines as a further application of the tellurium-based reducing system for aromatic nitro compounds.

A typical procedure is as follows: Under argon, to a stirred mixture of powdered tellurium (51 mg; 0.4 mmol) and sodium borohydride (1.52 g; 40 mmol) in ethanol (25 ml) was added all at once nitrobenzene (492 mg; 4 mmol) and the mixture was stirred at room temperature (22 °C) for 1.5 h. Then, under bubbling of argon, the mixture was poured into ice-water and acidified to pH 6 with 10% hydrochloric acid, and immediately extracted with ether. The extract was washed with brine and dried over anhydrous magnesium sulfate. After evaporation of the solvent under reduced pressure at room temperature, the crude product was purified by a short column chromatography (silica gel, methylene chloride) and subsequent recrystallization (benzene-petroleum ether) to give *N*-phenylhydroxylamine[5] (274 mg, 63%, mp 80-82 °C).

Several examples are given in Table 1. All reactions proceeded cleanly and completely in the presence of 10 mol% of tellurium to afford the corresponding hydroxylamines in 63-92% isolated yields. No formation of over-reduction products was discernible. It is known that some of hydroxylamines are labile. Lower yields of the products (**2a**, **2b**, **2c**, and **2g**) are the result of partial decomposition in work-up. Especially, the product (**2g**) was extremely labile for isolation in a pure state and was characterized by further converting into the corresponding *N*-hydroxybenzamide.[6,7] In the absence of tellurium, the reduction scarcely proceeded under the same reaction conditions (0-17%).

On the other hand, sodium hydrogentelluride,[8] prepared *in situ* from tellurium and sodium borohydride in a 1:2.4 molar ratio, has been used for the trans-

Table 1. Synthesis of *N*-Arylhydroxylamines[a]



	Nitro compound X	Reaction time/h	Hydroxylamine[b] Isolated yield/%[c]
a	H	1.5	63[d]
b	Me	3.0	65[d]
c	Cl	1.0	63[d]
d	CO_2Et	0.25	92[e]
e	CN	0.5	91[e]
f	NO_2	0.5	83[e,f]
g	$CH=CHCO_2Et$	1.0	74[e,g]

a) All reactions were carried out on 4 mmol scales with the same procedure as described in the text and no starting materials were recovered. b) All products except for **2g** (see ref. 6) were identified by direct comparison with authentic samples. c) Yields based on **1** used. d) Yields by recrystallization from benzene-petroleum ether. e) Yields by chromatography on silica gel. f) A mixed solvent of ethanol-water (25 ml, 1:1, v/v) was used instead of ethanol. g) Yield of the purified *N*-hydroxybenzamide after *N*-benzoylation of **2g**.

formation of nitrobenzenes into azoxybenzenes.[2] Under alkaline conditions (NaOH, 60 mmol), sodium hydrogentelluride (30 mmol) reduced nitrobenzene (4.0 mmol) to *N*-phenylhydroxylamine in 60% yield without the formation of azoxybenzene.[9] This method is also expected to open an alternative access to the synthesis of *N*-arylhydroxylamines.

N-Arylhydroxylamines have served as useful intermediates for the elaboration of nitrogen-containing heterocyclic compounds.[10] The present tellurium-catalyzed reduction provides a new entry to the selective synthesis of *N*-arylhydroxylamines[7] and has the advantages of ready accessibility of products, absence of side reactions, good yields, and experimental simplicity.

References

1) For a more recent review, see L. Engman, Acc. Chem. Res., 18, 274 (1985).
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5) O. Kamm, Org. Synth., Coll. Vol. I, 445 (1941).
6) The *N*-benzoylation product of **2g**, *N*-(4-(2-ethoxycarbonylvinyl)phenyl)-*N*-hydroxybenzamide, was prepared by the literature procedure.[7] Mp 130-131 °C (from benzene); Found: C, 69.46; H, 5.50; N, 4.46%. Calcd for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50; N, 4.50%.
7) For a recent paper on *N*-arylhydroxylamines synthesis, see N.R. Ayyangar, K.C. Brahme, U.R. Kalkote, and K.V. Srinivasan, Synthesis, 1984, 938.
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