

REDUCTION OF AROMATIC NITRO COMPOUNDS WITH SODIUM TELLURIDE

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Sodium telluride, prepared by heating tellurium with Rongalite in aqueous sodium hydroxide, easily reduces aromatic nitro compounds to the corresponding amines in good yields. The reduction can be carried out using a catalytic amount of tellurium, since sodium telluride is readily regenerated in the presence of excess Rongalite.

On heating with an excess of Rongalite ($\text{HOCH}_2\text{SO}_2\text{Na} \cdot 2 \text{H}_2\text{O}$) in dilute aqueous sodium hydroxide under nitrogen, tellurium is reduced to give sodium telluride as a wine-colored solution.¹⁾ Recently, we have reported that the reagent can effectively debrominate *vic*-dibromides to olefins²⁾ and tellurate nonactivated aryl iodides to form symmetrical diaryl tellurides.³⁾ As part of our investigations of synthetic utility of the tellurium/Rongalite system, we now wish to disclose that the same reagent can effect a facile reduction of nitrobenzenes (1) to anilines (2) under mild conditions.

When a nitro compound 1 was added to an aqueous solution of sodium telluride at 50-70 °C, reduction occurred rapidly with separation of free tellurium. Insoluble inorganic material was removed by filtration and the filtrate was worked up as usual to give amine 2 in a good yield. There was no indication of the formation of intermediate reduction products. The present reaction contrasts to the reduction using sodium hydrogentelluride (NaHTe), where azoxybenzenes are the major product.^{4,5)}

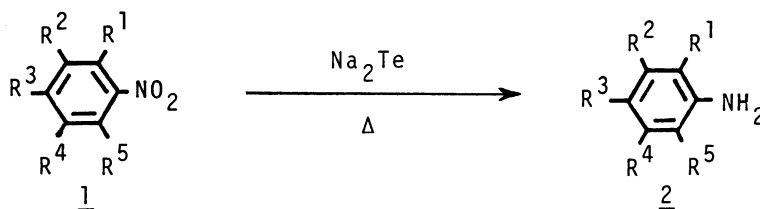


Table 1. Aromatic amines 2 obtained by the reduction of nitro compounds 1

	Nitro compound <u>1</u>					Reaction time/h	Aromatic amine <u>2</u> Yield/% ^{a)}
	R ¹	R ²	R ³	R ⁴	R ⁵		
a	CH ₃	H	CH ₃	H	CH ₃	2	95
b	CH ₃	CH ₃	CH ₃	CH ₃	H	2	87
c	CH ₃	H	(CH ₃) ₃ C	H	CH ₃	1	83
d	H	H	C ₆ H ₅	H	H	3	66
e	C ₆ H ₅	H	H	H	H	2	74
f	H	H	C ₆ H ₅ CO	H	H	1	90
g	H	H	C ₆ H ₅ CH=CH ^{b)}	H	H	1	78
h	-(CH=CH) ₂ -		H	H	H	2	55
i	CH ₃	CH ₃	NO ₂	CH ₃	CH ₃	3	89
j	NO ₂	CH ₃	CH ₃	CH ₃	CH ₃	3	96

a) Yields refer to the isolated compounds and do not represent optimized values. Products are all known, and identified by ¹H NMR, IR, and mass spectra as well as by direct comparison with authentic specimens.

b) *Trans*-isomer.

The reduction was found to be feasible using tellurium as a catalyst. Thus, when nitrobenzenes 1a-1h were allowed to react with excess of Rongalite in the presence of a small amount of tellurium in a 1M-sodium hydroxide solution/dioxane (5:1) mixture under nitrogen, the corresponding amines 2a-2h were obtained in 55-95% isolated yields (Table 1). The reaction proceeded cleanly without complications arising from the formation of bimolecular reaction products such as azo, azoxy, and hydrazo compounds. Hindered nitrobenzenes 1a and 1c were also smoothly converted to anilines 2a and 2c. Without tellurium, the conversion was too slow to be synthetically useful. Excess reducing agent was easily destroyed by exposing the reaction mixture to air.

The present method appears to be of general applicability. Polynitro compounds were reduced with similar ease to polyamines in the presence of excess Rongalite; dinitrobenzenes 1i-1j gave the corresponding diamines in 90-93% yields. When two nitro groups of substrate are in *ortho* or *para* relationship each other, the reaction could be stopped at the nitroamine stage by controlling the amount of

reducing agent; dinitrobenzenes $\underline{1i-1j}$ afforded $\underline{2i-2j}$ in 96 and 89% yields respectively. Dinitrobenzenes in which two nitro groups occupy the position *meta* to each other are susceptible to complete reduction and do not afford partially reduced products.

Reduction of aromatic nitro compounds under alkaline conditions usually leads to azobenzenes, azoxybenzenes, and/or hydrazobenzenes via combination of two molecules of the reduction intermediates.⁶⁾ While the method based on negative divalent sulfur has long been known for converting directly nitro compounds to amines in basic media,⁷⁾ the outcome of the reduction is not always easy to predict due to competing side reactions. The tellurium-mediated reduction of nitrobenzenes with Rongalite proceeds straightforward to anilines and may be used with sensitive compounds that would not be compatible with acid media, so it appears to be good alternative to the known methods for the reduction of aromatic nitro compounds.

The general procedure is as follows: Tellurium powder (0.013 g, 0.10 mmol) and Rongalite (0.77 g, 5 mmol) were placed in a reaction vessel and the system was thoroughly flushed with nitrogen. 1M-Sodium hydroxide solution (15 ml) followed by nitro compound (1.0 mmol) in dioxane (3 ml) was then introduced and the heterogeneous mixture was stirred at 50 °C for 1-3 h. The progress of the reaction was monitored by TLC. After an appropriate hour, by which time nitro compound $\underline{1}$ had almost completely disappeared, the reaction was quenched by allowing the mixture open to air. Sodium chloride (3-4 g) and chloroform (15-20 ml) were added with stirring and the mixture was freed from insoluble inorganic materials by filtration over a thin layer of Celite. The organic phase was separated and the aqueous solution was extracted with chloroform. The combined chloroform solutions were washed with brine, dried over sodium sulfate, and evaporated to give amine $\underline{2}$ as an oil or a solid residue.

Dinitro compounds could be similarly reduced to diamines by using twice the amount of reducing agent, increasing the proportion of dioxane in the solvent system, and extracting the product from aqueous solution with ether. Much longer reaction time (5-7 h) was needed for complete reduction.

References

- 1) L. Tschugaeff and W. Chlopin, Chem. Ber., 47, 1269 (1914). The characteristic coloring of the solution is attributed to the presence of polytelluride anions Te_n^{2-} .

- 2) H. Suzuki and M. Inouye, Chem. Lett., 1985, 225.
- 3) H. Suzuki and M. Inouye, Chem. Lett., 1985, 389.
- 4) A. Osuka, H. Shimizu, and H. Suzuki, Chem. Lett., 1983, 1373.
- 5) Sodium telluride can also be prepared by heating a 1:2 molar mixture of tellurium and sodium hydride in DMF under nitrogen. Under such aprotic conditions, sodium telluride converts nitrobenzene to azobenzene in high yields. Attempts to reduce nitrotoluenes, however, led to complicated mixtures of products arising from abstraction of benzylic hydrogen atom as well as partial reduction of nitro group. Bis(N,N-dimethylcarbamoyl) ditelluride (3), $(\text{H}_3\text{C})_2\text{NC}(=\text{O})\text{TeTeC}(=\text{O})\text{N}(\text{CH}_3)_2$, was obtained as a common by-product. A typical procedure for converting nitrobenzene to azobenzene is as follows: Tellurium powder (0.256 g, 2.0 mmol) and sodium hydride (0.10 g, 4.3 mmol; commercial 60% dispersion was washed with hexane prior to use) were placed in a reaction vessel, which was thoroughly flushed with nitrogen. Dry DMF (3 ml) was introduced and the mixture was heated at 140 °C for 1 h. To the resulting pale yellow suspension was added nitrobenzene (0.123 g, 1.0 mmol) in THF (2 ml), and the mixture was stirred at 60 °C for 4 h, by which time the substrate had almost completely disappeared. The reaction was quenched by bubbling air into the mixture, to which were then added a saturated sodium chloride solution (20 ml) and ether (20 ml). The mixture was freed from insoluble material by filtration on a thin layer of Celite, and the organic phase was separated and evaporated to a small volume. Addition of hexane to the concentrate precipitated ditelluride 3 (0.033-0.051 g; 7-16%) as fine yellow needles, which begins to darken at 118 °C and decomposes at 121-122 °C with liberation of tellurium. In solid state this compound could be stored for weeks in the dark, but in a solution it readily decomposed. ^1H NMR (CDCl_3), δ 3.12; IR (KBr), 1655, 1350, 1245, 1075, 870, and 660 cm^{-1} . Found: C, 18.62; H, 3.04; N, 7.02%. Calcd for $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_2\text{Te}_2$: C, 18.04; H, 3.03; N, 7.02%. Evaporation of the mother liquor and subsequent chromatography of the residual solid on a short silica gel column afforded azobenzene (0.082-0.088 g, 90-97%).
- 6) M. Hudlicky, "Reductions in Organic Chemistry," Ellis Horwood Ltd., Chichester (1984), pp 71-74.
- 7) Generally, ammonium, sodium, or potassium sulfide, hydrosulfide, or polysulfide are used as the reagents in aqueous, alcoholic, or liquid ammoniac media.

(Received August 22, 1985)