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Reduction of Aromatic Nitro Compounds and Thioketones with Sodium Telluride under Aprotic Conditions

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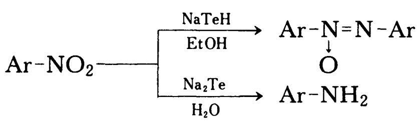
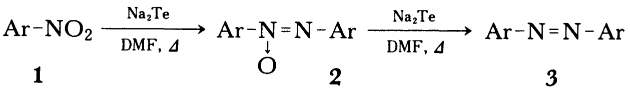
Synopsis. Sodium telluride, prepared by heating tellurium and sodium hydride in a 1 : 2 molar ratio in dry *N,N*-dimethylformamide, reduces aromatic nitro compounds to azo compounds and thioketones to hydrocarbons under mild conditions.

Hydrogen telluride is a weak dibasic Brϕnsted acid and forms two series of salts known as hydrogentelluride $M^{I}TeH$ and normal telluride M^{I}_2Te. Salts of the former type undergo transformation into those of second type in high pH region. Recently, we reported that aromatic nitro compounds behave differently toward these telluride reagents; sodium telluride easily reduces nitrobenzenes to anilines,[1] while sodium hydrogentelluride does not reduce them beyond the stage of azoxy compounds.[2] Both of these types of reductions proceed cleanly in protic media and are complete within a short reaction time under mild conditions. The reduction with sodium hydrogentelluride is sensitive to steric factor as evidenced by the formation of anilines where nitrobenzenes are hindered.[2]



As part of our studies on telluride reduction, we report herein that aromatic nitro compounds undergo another type of reaction with sodium telluride under aprotic conditions, giving not azoxy but azo compounds as the single product. Sodium telluride was also found to effect reductive removal of sulfur atom from aromatic thioketones to yield parent hydrocarbons.

On heating gently with sodium hydride in dry *N,N*-dimethylformamide (DMF) under nitrogen, powdered tellurium dissolved with evolution of hydrogen gas to form a deep red solution of sodium oligotelluride, which on further heating gradually lost color to give sodium telluride as a pale yellow suspension. When a nitroarene (**1**) dissolved in tetrahydrofuran (THF) was added to the suspension and the resulting mixture was heated with stirring at around 70 °C for several hours, smooth reduction took place to give the corresponding azo compound (**3**) in good to moderate yields (Table 1).

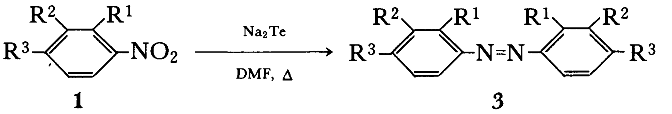


The reaction proceeded cleanly with nitroarenes **1a**—**e** and halonitroarenes **1f**—**g**. The intermediary azoxy compounds (**2**) are too reactive to be isolated under these conditions, although they can be detected in certain cases at an early stage of reduction. A similar reaction of 4-nitrotoluene led to a complex mixture of products arising from abstraction of benzylic hydrogen atom as well as partial reduction of nitro group. Isolation of 1,2-bis(4-nitrophenyl)ethane as one of products revealed the intervention of radical species in the reduction under aprotic conditions. As expected, 3-nitrotoluene **1b** gave azobenzene **3b**. In every case, bis(dimethylcarbamoyl) ditelluride (**4**) was obtained as a common by-product. We attributed the formation of **4** to capture of the initially formed dimethylcarbamoyl radical by telluride anion and subsequent oxidation of the resulting tellurocarbamoyl species. This type of reaction is of interest since it may represent the formal oxidation of DMF to a telluro analog of dimethylcarbamoyl peroxide.

$$(H_3C)_2NCHO \xrightarrow{-H\cdot} (H_3C)_2N\dot{C}(=O) \xrightarrow[-2e]{Te^{2-}}$$

$$(H_3C)_2NC(=O)Te\cdot \longrightarrow \underset{\mathbf{4}}{(H_3C)_2NC(=O)TeTeC(=O)N(CH_3)_2}$$

Table 1. Reduction of Aromatic Nitro Compounds with Sodium Telluride

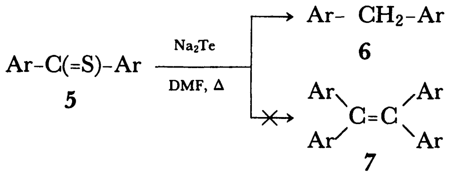


1 3

	Nitroarene 1			Azo compound 3	
	R^1	R^2	R^3	Mp(θ_m/°C)	Yield/%[a)]
a	H	H	H	68—69 (67—68)[6)]	97
b	H	CH_3	H	50—52 (54—55)[7)]	62
c	C_6H_5	H	H	141—143 (144—145)[8)]	75
d	H	H	C_6H_5	245—249 (248—250)[7)]	70
e	-(CH=CH)$_2$-		H	194—196 (197—198)[7)]	78
f	H	Cl	H	98—101 (103—104)[7)]	87
g	H	H	Cl	185—188 (186—188)[6)]	67

a) Yields refer to the isolated compounds and are not optimized.

Treatment of aromatic thioketones (**5**) with sodium telluride in aqueous media resulted in the generation of original ketones. Under aprotic conditions, however, the same reagent was found to desulfurize thioketones **5** in a reductive way to afford the corresponding hydrocarbons (**6**). The reaction proceeded slowly and the only predominant product was parent hydrocarbon **6**. Dimerization with loss of sulfur leading to tetraarylethylene (**7**), an important process in the reduction of thioketones with diphosphorus tetraiodide,[3] could not be observed.



Experimental

Melting points were determined on a hot stage apparatus and are not corrected. Powdered tellurium (99.9% purity) and sodium hydride (60% dispersion in oil) were commercial products and used as received. Thioketones were prepared from the corresponding ketones by known method.[4] Reactions were performed under nitrogen to protect sodium telluride from oxidation. All products except ditelluride **4** are known and identified by direct comparison with authentic samples obtained by other routes.

Preparation of Sodium Telluride. A mixture of powdered tellurium (0.256 g, 2.0 mmol), sodium hydride (0.10 g, 4.2 mmol; washed thoroughly with hexane prior to use), and DMF (3 ml) was stirred at 140 °C for 1 h under nitrogen. As the tellurium went into solution, hydrogen was evolved and a deep red color developed within 10—15 min. After 1 h, the color faded and the mixture turned to a pale yellow suspension of sodium telluride, which was immediately used for reduction. On contact with air, sodium telluride rapidly decomposes with liberation of elemental tellurium.

Reduction of Aromatic Nitro Compound to Azo Compound. To a stirred suspension of sodium telluride (2.0 mmol) in DMF (3 ml), a solution of nitroarene (**1**; 1.0 mmol) in THF (2 ml) was added by cannula at room temperature under nitrogen. The mixture was gently heated to 70 °C and kept at this temperature for 3—5 h. Progress of the reaction was monitored by TLC on silica. The reaction was quenched by bubbling air into the mixture, to which was then added a saturated sodium chloride solution (20 ml) followed by ether (20 ml). The insoluble material was filtered through a thin layer of Celite and the organic phase was separated from the filtrate, washed with 10% hydrochloric acid to remove any DMF, and evaporated to leave a crude azo compound **3**, which was purified by chromatography on silica gel or recrystallization from appropriate solvent.

Isolation of Bis(dimethylcarbamoyl) Ditelluride (4). The reaction mixture was worked up as described above. Without being washed with 10% hydrochloric acid, the ethereal extract was evaporated to a small volume. Hexane was added to the concentrate and the mixture was left to stand in a refrigerator. Ditelluride **4** separated as fine yellow needles, which begins to darken at 118 °C and decomposes at 121—122 °C with liberation of tellurium. Yields were variable, usually in the range of 5—15%. In solid state this compound could be stored for weeks in the dark, but in a solution it readily decomposed. ^{1}H NMR ($CDCl_3$) δ=3.12 (12H, s, CH_3); IR (KBr disk) 1655,1350, 1245, 1075, 870, and 660 cm^{-1}. Found: C, 18.62; H, 3.04; N, 7.02%. Calcd for $C_6H_{12}N_2O_2Te_2$: C, 18.04; H, 3.03; N, 7.02%.

Reductive Desulfurization of Aromatic Thioketones to Parent Hydrocarbons. Typical Procedure: To a suspension of sodium telluride (2.0 mmol) in DMF (3 ml) was added xanthene-9-thione (0.210 g, 1.0 mmol) in THF (5 ml) and the resulting mixture was heated under gentle reflux. The color changed from green to orange to blue, and finally to black. After 2 d excess sodium telluride was destroyed by exposing to air and water (20 ml) followed by dichloromethane (20 ml) was added. The insoluble material was removed by filtration on a thin layer of Celite, and the organic phase was separated from the filtrate, washed with 10% hydrochloric acid, and evaporated. The residue was chromatographed on silica gel to afford xanthene (0. 161 g, 82%). Mp 96—99 °C (lit,[5] 100 °C).

Under similar conditions, thiobenzophenone and 4-bromothiobenzophenone were reduced to diphenylmethane and 4-bromodiphenylmethane, respectively, in 60—70% isolated yields.

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