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A Facile Displacement of Tertiary Nitro Group by Hydrogen with Sodium Hydrogentelluride

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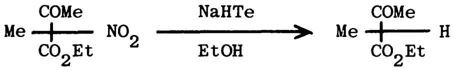
Synopsis. Sodium hydrogentelluride is a useful reagent for replacement of a class of tertiary nitro group by hydrogen.

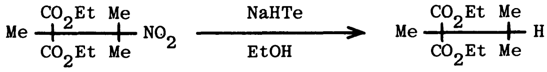
In recent years, reductive removal of nitro group from nitroalkanes has been the subject of extensive investigation in connection with the versatile utilities of nitroalkanes in organic syntheses, which have been well demonstrated in the last two decades.[1] As a result, several methods have been developed to bring about such a conversion — a) sodium salt of methanethiol in dipolar aprotic solvents,[2] b) potassium hydroxide in ethylene glycol,[3] c) *N*-benzyl-1,4-dihydronicotinamide,[4] and d) tributyltin hydride in the presence of azobis-isobutyronitrile.[5] However, these methods have certain drawbacks such as the necessity of high temperature (method a, b, and c), long reaction time (method a), and chromatographic separation (method d), the formation of side products (method a), or the incompatibility of other functional groups (method b).

Herein we disclose the results of our new procedure for the replacement of tertiary nitro group by hydrogen through the use of sodium hydrogentelluride (NaHTe).[6] The experimental procedure is marked by its simplicity in that it involves just the treatment of nitro compounds with NaHTe in ethanol for 15 min at room temperature.



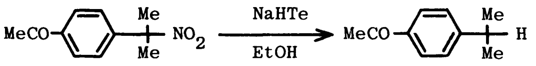
$$\mathrm{Me{-}C(COMe)(CO_2Et){-}NO_2 \xrightarrow[EtOH]{NaHTe} Me{-}C(COMe)(CO_2Et){-}H}\quad (100\%) \qquad (1)$$

1 **2**



$$\mathrm{Me{-}C(CO_2Et)_2{-}CMe_2{-}NO_2 \xrightarrow[EtOH]{NaHTe} Me{-}C(CO_2Et)_2{-}CMe_2{-}H}\quad (98\%) \qquad (2)$$

3 **4**

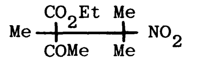
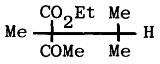
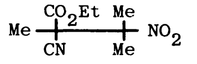
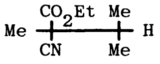
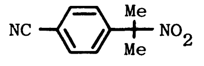
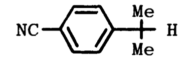
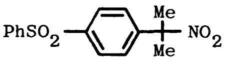
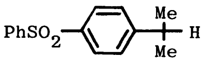
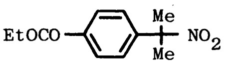
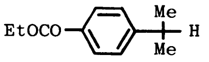


$$\mathrm{MeCO{-}C_6H_4{-}CMe_2{-}NO_2 \xrightarrow[EtOH]{NaHTe} MeCO{-}C_6H_4{-}CMe_2{-}H}\quad (85\%) \qquad (3)$$

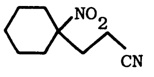
9 **10**

Tertiary nitro group at α or β-position of ketone and ester was readily replaced by hydrogen (Eqs. 1 and 2). Similarly, α-nitrocumene derivative **9** was transformed into the corresponding 4-substituted cumene **10** in 85% yield (Eq. 3). Other examples were listed in Table 1. It should be noted that the isolated yields were excellent, the chromatographic separation was unnecessary, and other functional groups such as keto, cyano, ester, and sulfonyl groups remained unaffected under the present conditions.

TABLE 1. REPLACEMENT OF TERTIARY NITRO GROUP BY HYDROGEN WITH SODIUM HYDROGENTELLURIDE (NaHTe)[a]

Reactant		Product		Yield/%[b]
 $\mathrm{Me{-}C(CO_2Et)(COMe){-}CMe_2{-}NO_2}$	**5**	 $\mathrm{Me{-}C(CO_2Et)(COMe){-}CMe_2{-}H}$	**6**	96
 $\mathrm{Me{-}C(CO_2Et)(CN){-}CMe_2{-}NO_2}$	**7**	 $\mathrm{Me{-}C(CO_2Et)(CN){-}CMe_2{-}H}$	**8**	95
	**11**		**12**	80
	**13**		**14**	81
	**15**		**16**	87

a) All reactions were performed as described in detail in the text. b) Values reported are isolated ones.



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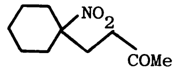

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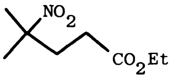
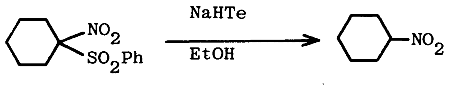


19

However, to our surprise, nitro compounds, **17**, **18**, and **19** in which nitro group is situated at γ-position of ketone, ester, and nitrile, were quantitatively recovered after prolonged treatment with NaHTe even at refluxing conditions in ethanol. Finally, the reaction of 1-nitro-1-(phenylsulfonyl)cyclohexane **20** with NaHTe gave rise to the replacement of phenylsulfonyl group, instead of nitro group, by hydrogen (Eq. 4).



(100%) (4)

20 **21**

Although the reaction mechanism has not been studied yet, it appears to involve one-electron transfer to the nitro compound from NaHTe and the subsequent detachment of nitrite anion from the resulting nitro compound anion radical. Thus, in the case of compound **20**, phenylsulfonyl group which is a better leaving group than nitro group, was preferentially cleaved from the anion radical intermediate over nitro group.[8] In addition, the reluctance of nitro compounds **17**, **18**, and **19** toward NaHTe might be ascribed to the failure of the initial electron transfer from NaHTe to these compounds.

Experimental

Tertiary nitro compounds were prepared according to

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the reported procedure.[7)]

General Procedure for the Replacement of Tertiary Nitro Group by Hydrogen with Sodium Hydrogentelluride (NaHTe). A solution of tertiary nitro compound (4 mmol) in ethanol (4 ml) was added at room temperature under nitrogen atmosphere to a solution of NaHTe,[8)] prepared *in situ* by reacting tellurium powder (1.30 g, 10 mmol) and sodium borohydride (0.90 g, 24 mmol) for 1 h in refluxing ethanol (40 ml). An instantaneous reaction occurred and the color of the reaction mixture changed to deep black. After 15 min, water (50 ml) was added, and the resulting mixture was left open to air with stirring. The solution became clear after 1 h with the deposition of tellurium powder. It was then filtered through Celite 545 and the filtrate was extracted with three portions of dichloromethane (30 ml). The combined extracts were washed with water, dried over Na_2SO_4, and evaporated to give the crude product, which was purified by Kugelrohr distillation or recrystallization. The products were identified by comparison with authentic samples.

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