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REDUCTION OF AROMATIC AND ALIPHATIC NITRO COMPOUNDS BY SODIUM HYDROGEN TELLURIDE

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Various nitro compounds were effectively reduced by sodium hydrogen telluride in good yields. Thus, reductive conversion of unhindered nitrobenzenes to azoxybenzenes, sterically hindered nitrobenzenes to anilines, nitroalkanes to dimer of nitrosoalkanes, and vicinal-dinitroalkane to olefin was achieved.

Sodium hydrogen telluride (NaTeH), which is prepared from tellurium and sodium borohydride,1) has recently been used for several reductions such as the reduction of Vilsmeier salts,1) hydrogenation of activated carbon-carbon double bonds,2) and dehalogenation of vicinal-dihaloalkanes3) and α-halogeno-carbonyl compounds.4) In this letter we wish to report the reducing ability of NaTeH toward aromatic and aliphatic nitro compounds.

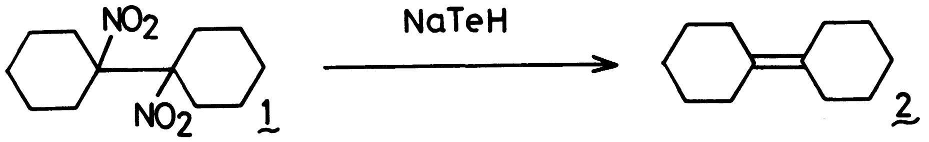
The experimental procedure is marked by its simplicity in that it involves just stirring the nitro compounds with 5 equiv. of NaTeH in ethanol for 1 h at room temperature. In general the aromatic nitro compounds were reduced to azoxybenzenes in good yields (Table 1). However, in the case of hindered compounds such as 2,4,6-trimethylnitrobenzene and 2,6-dimethyl-4-tert-butylnitrobenzene, the corresponding anilines were obtained. Apparently the condensation of intermediate nitrosobenzene with phenylhydroxylamine was prohibited sterically. It is interesting to note that the carbonyl group in 4-nitroacetophenone remained unaffected during the reaction. Azoxybenzene itself gave hydrazobenzene quantitatively under the same conditions. Recently hydrogen telluride (H_2Te) prepared from Al_2Te_3 and H_2O has been reported to reduce the aromatic nitro compounds to the anilines.5) Thus, it may be said that NaTeH is a milder reducing reagent than H_2Te.

Recently, the reductive elimination of nitro group from alipahtic nitro compounds has attracted considerable interest in connection with their uses in

Table 1. Reduction of Aromatic Nitro Compounds by NaTeH

Reactant	Yield/%[a)	Reactant	Yield/%[a)
	$\text{Ar-N=}\underset{\substack{\downarrow\\ \text{O}}}{\text{N}}\text{-Ar}$		$\text{Ar-N=}\underset{\substack{\downarrow\\ \text{O}}}{\text{N}}\text{-Ar}$
$C_6H_5NO_2$	65	$4\text{-ClC}_6H_4NO_2$	82
$2\text{-MeC}_6H_4NO_2$	82	$4\text{-BrC}_6H_4NO_2$	86
$4\text{-MeC}_6H_4NO_2$	92	$4\text{-MeCOC}_6H_4NO_2$	66
$4\text{-MeOC}_6H_4NO_2$	66	$2,4,6\text{-Me}_3C_6H_2NO_2$	-[b)
$2\text{-ClC}_6H_4NO_2$	63	$2,6\text{-Me}_2\text{-4-Bu}^tC_6H_2NO_2$	-[c)
$3\text{-ClC}_6H_4NO_2$	72		

[a) Isolated yields. [b) 2,4,6-Trimethylaniline (92%) was obtained. [c) 2,6-Dimethyl-4-tert-butylaniline (89%) was obtained.



organic syntheses.[6) It was therefore our interest to investigate the reduction of nitroalkanes with NaTeH. When the reduction was performed on nitrocyclohexane and 1-nitroheptane, they were reduced only to their nitrosoalkane dimers, namely N,N'-dicyclohexyldiazene N,N'-dioxide and N,N'-diheptyldiazene N,N'-dioxide in 80 and 66% yields, respectively. However, the reductive elimination of the nitro group was succesfully accomplished when a vicinal-dinitro compound, 1-nitro-1-(1-nitrocyclohexyl)cyclohexane (1), was reacted with NaTeH to give cyclohexylidenecyclohexane (2) in 86% yield.

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