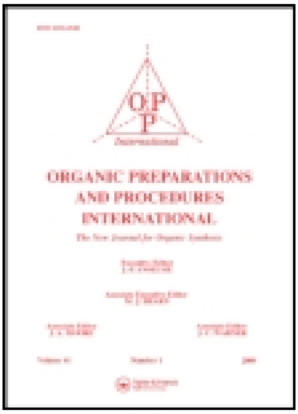

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Facile Deoxygenation of Telluroxides, Tellurones and Selenones with Nickel Boride at Ambient Temperature

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Facile Deoxygenation of Telluroxides, Tellurones and Selenones with Nickel Boride at Ambient Temperature

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Nickel boride has been reported as a convenient and efficient reagent in numerous transformations.[1–5] It is superior to many other metal catalysts due to its low cost, ease of preparation and handling, non-pyrophoric nature and easy removal. Unlike its initial applications as a heterogeneous catalyst, nickel boride is used as a reducing agent without aid of hydrogen as it contains adsorbed hydrogen.[1] Nickel boride, prepared *in situ*, has been reported for a variety of applications such as, reductions,[6] deoxygenations,[7] desulfurizations,[8] etc. In continuation of our studies on the deoxygenation of sulfoxides and selenoxides,[9] and in view of the paucity of the reagents for the deoxygenation of chalcogenide monoxides[10–12] and especially chalcogenide dioxides,[13] we attempted to develop new methodologies using nickel boride and now report the deoxygenation of aryl, alkyl and aralkyl telluroxides, tellurones and selenones with nickel boride generated *in situ* from nickel(II) chloride and sodium borohydride in different solvents at ambient temperature to give the corresponding tellurides and selenides respectively.

Di(4-tolyl)telluroxide (**1a**) was chosen as a model substrate to investigate and optimize the conditions for the deoxygenation. The reactions were carried with nickel boride generated *in situ* in different solvents such as MeOH, THF, DMF and dioxane, and in different molar ratios of substrate to nickel boride. It was observed that deoxygenation of di(4-tolyl)telluroxide could be achieved with anhydrous $NiCl_2$ and sodium borohydride in dry THF using 1:1:3 molar ratio of substrate:$NiCl_2$:$NaBH_4$ at ambient temperature to give 86% of di(4-tolyl)telluride (**2a**). The protocol was then extended to a variety of aryl, alkyl and aralkyl telluroxides. All the telluroxides underwent deoxygenation to give corresponding tellurides in high yields (*Table 1*). Halo substituents were unaffected under these

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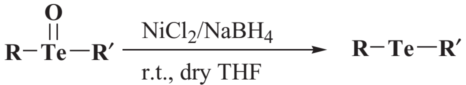
Table 1

Deoxygenation of Telluroxides (***1a–g***) with Nickel Boride[a]

Substrate (s)	Product	Yield (%)	mp (°C)	lit. mp (°C)	Time (min)
1a	***2a***	86	66–68	64–65[14]	10
1b	***2b***	87	54–56	54–55[14]	15
1c	***2c***	84	116–120	118–120[15]	75
1d	***2d***	82	90–92	89–90[16]	180
1e	***2e***	78	Liquid	Liquid[23]	120
1f	***2f***	80	Liquid	Liquid[13]	60
1g	***2g***	85	68–70	-	15

a) Ratio of substrate:$NiCl_2$:$NaBH_4$ is 1:1:3 except for ***1d*** which is 1:2:6.

conditions (*Eq. 1*).



$$\underset{\mathit{1}}{R{-}\overset{\overset{\displaystyle O}{\|}}{Te}{-}R'} \xrightarrow[\text{r.t., dry THF}]{NiCl_2/NaBH_4} \underset{\mathit{2}}{R{-}Te{-}R'} \qquad (1)$$

a) $R = R' = 4\text{-}MeC_6H_4$ b) $R = R' = 4\text{-}OMeC_6H_4$ c) $R = R' = 4\text{-}BrC_6H_4$
d) $R = R' = 4\text{-}ClC_6H_4$ e) $R = R' = C_4H_9$ f) $R = C_6H_5$, $R' = Me$
g) $R = R' = MeO_2CC_6H_4$

While the reactions of di(4-tolyl)telluroxide (**1a**) in dioxane and DMF were sluggish, reaction in dry MeOH using molar ratios 1:1:3 of substrate:$NiCl_2$:$NaBH_4$ was complete in 3 min but yielded only 44% of di(4-tolyl)telluride (**2a**); this could be due to the formation of detellurized product as well. The reaction of di(4-carbomethoxyphenyl)telluroxide (**1g**) under above conditions (*i.e* molar ratio 1:1:3 of substrate:$NiCl_2$:$NaBH_4$ in dry MeOH) yielded di(4-carbomethoxyphenyl)telluride (**2g**) (42%) and methyl benzoate (45%) (*Eq. 2*). However, methyl benzoate was not formed when the reaction was carried out in dry THF. This result suggests that detellurization is competing with deoxygenation when the reaction is carried out in methanol. This is possibly due to the enhanced reactivity of nickel boride in protic solvent (MeOH) as compared to aprotic solvent (THF).

$$\underset{\mathit{1g}}{4\text{-}(MeO_2CC_6H_4)_2Te{=}O} \xrightarrow[\text{r.t., MeOH}]{NiCl_2/NaBH_4} \underset{\mathit{2g}}{4\text{-}(MeO_2CC_6H_4)_2Te} + PhCO_2Me \qquad (2)$$

The scope of the reagent was also investigated for the deoxygenation of tellurones, selenones and sulfones. The reactions of di(4-tolyl)tellurone (**3a**) and diphenyl selenone (**3g**) were carried out under the optimized conditions used for telluroxides but deoxygenation was incomplete even with higher molar ratios of catalyst to substrate:$NiCl_2$:$NaBH_4$ (1:5:15). The reactions were then attempted in different solvents at different temperatures using varying molar ratios of substrate to nickel boride to achieve the complete

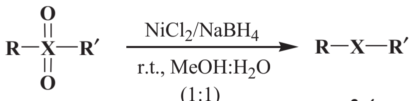
Table 2

Deoxygenation of Tellurones (***3a–o***) and Selenones with Nickel Boride[a]

Substrate (s)	Product	Yield (%)	mp (°C)	lit. mp (°C)	Time (min)
3a	***2a***	83	66–68	64–65[14]	10
3b	***2b***	84	54–56	54–55[14]	25
3c	***2c***	79	116–118	118–120[15]	15
3d	***2d***	76	90–92	89–90[16]	20
3e	***2e***	79	Liquid	Liquid[23]	10
3f	***2f***	78	Liquid	Liquid[13]	20
3g	***4g***	88	Liquid	Liquid[16]	20
3h	***4h***	86	40–42	44[13]	120
3i	***4i***	82	66–68	69[13]	60
3j	***4j***	84	52–54	55–56[13]	60
3k	***4k***	84	94–96	95–96[13]	120
3l	***4l***	85	112–114	114–115[13]	60
3m	***4m***	75	Liquid	Liquid[18]	120
3n	***4n***	83	Liquid	Liquid[18]	180
3o	***4o***	84	Liquid	Liquid[13]	180

a) Ratio of substrate:$NiCl_2$:$NaBH_4$ is 1:1:3 except for ***3h*** and ***3o*** which is 1:2:6.

deoxygenation. $MeOH$:H_2O (1:1, v/v) was found to be the solvent of choice. Deoxygenations of di(4-tolyl)tellurone (**3a**) and diphenyl selenone (**3g**) were complete with a 1:1:3 molar ratio of substrate:$NiCl_2$:$NaBH_4$ in $MeOH$:H_2O (1:1) at ambient temperature leading, to high yields of di(4-tolyl) telluride (**2a**) and diphenyl selenide (**4g**), respectively. Subsequently, various aryl, alkyl and aralkyl tellurones and selenones underwent deoxygenation in high yields to the corresponding tellurides and selenides in methanol:water (1:1, v/v) at ambient temperature (*Table 2*).



$$R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{X}}-R' \xrightarrow[\text{r.t., MeOH:H}_2\text{O (1:1)}]{NiCl_2/NaBH_4} R-X-R' \quad (3)$$

3 *2,4*

a) R = R′ = 4-MeC_6H_4, X = Te
b) R = R′ = 4-$OMeC_6H_4$, X = Te
c) R = R′ = 4-BrC_6H_4, X = Te
d) R = R′ = 4-ClC_6H_4, X = Te
e) R = R′ = C_4H_9, X = Te
f) R = C_6H_5, R' = Me, X = Te
g) R = R′ = C_6H_5, X = Se
h) R = R′ = $CH_2C_6H_5$, X = Se
i) R = R′ = 4-MeC_6H_4, X = Se
j) R = R′ = 4-$OMeC_6H_4$, X = Se
k) R = R′ = 4-ClC_6H_4, X = Se
l) R = R′= 4-BrC_6H_4, X = Se
m) R = R′ = C_4H_9, X = Se
n) R = R′ = $C_{12}H_{25}$, X = Se
o) R = C_3H_7, R′ = 4-MeC_6H_4, X = Se

No deselenized or detellurized products were obtained under these conditions. The amount of water plays a crucial role in the reaction. The use of higher amounts of water resulted in sluggish or incomplete reactions while lowering the amount of water resulted in the formation of a mixture of products. Sulfones were unaffected under these and all other conditions attempted by us.

Thus, we have developed a very efficient and a convenient method for the deoxygenation of telluroxides in dry THF, selenones and tellurones in MeOH-H_2O (1:1) to the corresponding chalcogenides at ambient temperature using nickel boride generated *in situ*.

Experimental Section

All melting points were recorded on Tropical Labequip apparatus and are uncorrected. IR spectra were recorded on Perkin-Elmer FT-IR SPECTRUM-2000 and NMR spectra were obtained on Hitachi FT-NMR (60 MHz) and JEOL at 400 MHz using TMS as internal standard. Mass spectra were acquired on KC-455-TOF Mass Spectrometer (Micromass, Manchester, UK). THF (S. D. Fine), methanol (S. D. Fine), nickel chloride hexahydrate (S. D. Fine) and sodium borohydride (E. Merck) were used in all the reactions. Anhydrous Nickel(II) chloride was prepared by heating Nickel(II) chloride hexahydrate in a crucible till golden yellow. It was then allowed to cool at room temperature and stored over calcium chloride in a desiccator. Di(4-carbomethoxyphenyl)telluride and di(4-carbomethoxyphenyl) telluroxide were prepared by reported methods.[30–34] All the products, except di(4-carbomethoxyphenyl)telluride, are known and were identified by co-TLC with authentic samples and by mp, IR and NMR spectra which are in good agreement with reported literature.[14–29]

General Procedure of Deoxygenation of Telluroxides. In a typical experiment, di(4-tolyl)telluroxide (1 mmol, 0.325 g), anhydrous nickel chloride (1 mmol, 0.129 g) and dry THF (10 mL) with a stir bar and were placed in a 50 mL RB flask, fitted with a condenser and calcium chloride guard tube. Sodium borohydride (3 mmol, 0.114 g) was added to the mixture and the contents were stirred at room temperature. The progress of the reaction was monitored by TLC using petroleum ether:ethyl acetate (80:20, v/v) as eluent. After complete disappearance of the telluroxide, the reaction mixture was cooled to room temperature and filtered through a Celite pad (~2.5 cm). The nickel boride precipitate was washed with ethyl acetate (2 × 5 mL). Water (20 mL) was added to the filtrate, which was extracted with ethyl acetate (3 × 10 mL). The combined ethyl acetate extract was dried over anhydrous Na_2SO_4 and concentrated on a rotary evaporator to give a solid which after drying under vacuum, was characterized by its mp, IR and ^1H NMR spectra as di(4-tolyl)telluride (86%).

Di(4-Carbomethoxyphenyl)telluroxide (1g), mp. 168–170°C; IR(KBr): 2922, 1725, 1273, 1106, 730 cm^{-1}; ^1H-NMR ($CDCl_3$, 60 MHz, ppm): δ 3.9 (s, 6H, -OCH_3), 7.8–8.0 (m, 8H, Ar-H); ^{13}C NMR ($CDCl_3$, 400 MHz, ppm): δ 52.22, 129.53, 129.78, 130.36, 137.47, 166.72; MS (ESI) m/z 415.9859.

Anal. Calcd for $C_{16}H_{14}O_5Te$: C, 46.43; H, 3.41. Found: C, 46.62; H, 3.21.

Di(4-Carbomethoxyphenyl)telluride (2g), mp. 66–68°C; IR(KBr): 2925, 1723, 1584, 1284, 1104, 754, 471 cm^{-1}; ^1H-NMR($CDCl_3$, 60 MHz, ppm): δ 3.9 (s, 6H, -OCH_3), 7.8–7.8 (m, 8H, Ar-H); ^{13}C NMR ($CDCl_3$, 400 MHz, ppm): δ 52.22, 129.53, 129.78, 130.36, 137.47, 166.72; MS (ESI) m/z 400.0120.

Anal. Calcd for $C_{16}H_{14}O_4Te$: C, 48.30; H, 3.55; Found: C, 48.53; H, 3.41.

General Procedure of Deoxygenation of Tellurones/Selenones: In a typical reaction, to a solution of tellurone/selenone (1 mmol) in 10 mL of methanol:H_2O (1:1, v/v) in a 50 mL RB flask fitted with a condenser and magnetic stir bar, was added $NiCl_2.6H_2O$, followed by the cautious addition of $NaBH_4$. The reaction mixture was stirred vigorously at room temperature. After the completion of reaction as monitored by TLC, using $CHCl_3$:MeOH (60:40, v/v) as eluent, the reaction mixture was worked up as described above. The product was analyzed by comparison of their mp, IR and ^1H NMR spectra with those reported in literature.

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