

Sodium Benzenetellurolate-catalysed Selective Reduction of Aromatic Nitro Compounds to Azoxy Compounds

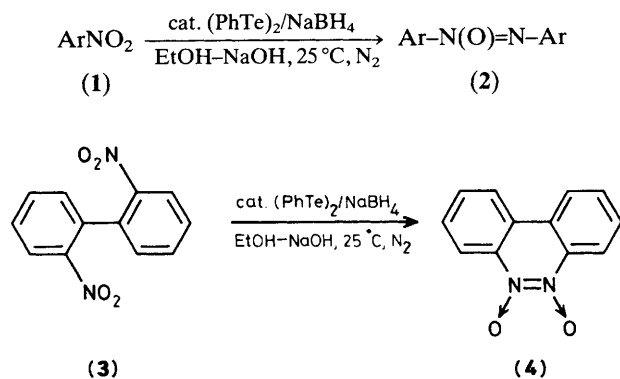
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Treatment of aromatic nitro compounds with sodium borohydride in alkaline ethanol in the presence of a catalytic amount of diphenyl ditelluride at 25 °C affords the corresponding azoxy compounds selectively in high yields, *in situ* generated sodium benzenetellurolate being the active species which produces the intermediate aromatic nitroso compounds.

Tellurium compounds such as H_2Te , NaTeH , Na_2Te , Li_2Te , and PhTeH have recently been introduced as mild and efficient reducing agents for various organic compounds and their catalytic use has also been developed.¹ Sodium arenetellurolates (ArTeNa) are produced by reduction of diaryl ditellurides by sodium borohydride (NaBH_4) in ethanol-

benzene in the presence of NaOH ,² but their use for reduction is limited to dehalogenation of several organic halides. We report here the first example of the catalytic use of sodium benzenetellurolate (PhTeNa) for the selective reduction of aromatic nitro compounds to the corresponding azoxy compounds.



When nitrobenzene (**1**; Ar = Ph) (2 mmol) was treated with NaBH₄ (10 mmol) and diphenyl ditelluride (0.5 mmol) in ethanol (15 ml) containing 5 M aqueous NaOH (2.5 ml) at 25 °C for 10 h under nitrogen, azoxybenzene (**2**; Ar = Ph) was obtained in 92% yield together with a trace of azobenzene. Aniline was not detected. Under the same conditions without diphenyl ditelluride no reduced products were formed, the nitrobenzene being recovered intact. Reduction with lower concentrations of NaOH or in its absence gave a mixture of (**2**), azobenzene, and aniline. Various substituted nitrobenzenes were also reduced to the corresponding azoxy compounds, typical results being shown in Table 1. The rate of reduction of (**1**) bearing an electron-donating group was generally slower than that of (**1**) bearing an electron-withdrawing group. The carbonyl group in *p*-nitroacetophenone (**1**; Ar = 4-MeCOC₆H₄) was also reduced to hydroxy. Since benzenetellurol (PhTeH) is known to reduce aromatic nitro compounds to the corresponding anilines in benzene/ethanol/water at 80 °C or to a mixture of (**2**) and the anilines at lower temperatures,⁴ our results show that PhTeNa is a milder reducing agent than PhTeH.[†]

Nitrosobenzene was reduced to (**2**; Ar = Ph) quantitatively under the conditions shown in Table 1, while (**2**; Ar = Ph) was not produced from phenylhydroxylamine. Since the reductive

[†] The reduction of (**1**; Ar = Ph) at reflux temperature under our conditions gave a mixture of (**2**) and azobenzene, aniline not being formed.

Table 1. Sodium benzenetellurolate-catalysed reduction of (**1**) to (**2**)^a.

Ar in (1)	(PhTe) ₂ (mmol)	Time/ h	Isolated yield of (2) (%) ^b
Ph	0.05	10	91(92)
<i>o</i> -MeC ₆ H ₄	0.05	40	78(91)
<i>m</i> -MeC ₆ H ₄	0.05	10	(83)
<i>p</i> -MeC ₆ H ₄	0.05	20	(85)
<i>p</i> -ClC ₆ H ₄	0.10	12	99
<i>p</i> -BrC ₆ H ₄	0.10	12	96
<i>p</i> -MeOC ₆ H ₄	0.10	40	60
<i>p</i> -MeCOC ₆ H ₄	0.05	7	82 ^c

^a Carried out with (**1**) (2 mmol) and NaBH₄ (10 mmol) in ethanol (15 ml) and 5 M aq. NaOH (2.5 ml) at 25 °C under nitrogen. ^b G.l.c. yield in parentheses. ^c Product: (**2**; Ar = *p*-MeCHOHC₆H₄).

coupling of nitrosobenzene to (**2**; Ar = Ph) occurred smoothly even in the absence of diphenyl ditelluride, PhTeNa appears to act by reducing (**1**) to the corresponding nitroso compounds. The almost quantitative formation of the intramolecular coupling compound (**4**)[‡] from *o,o'*-dinitrophenyl (**3**) also suggests the intervention of a nitroso compound as an intermediate.

Received, 19th January 1988; Com. 8/00192H

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[‡] M.p. 251–252 °C (from benzene–EtOH; lit.⁵ m.p. 233–236 °C); mass *m/z* 212 (*M*⁺); satisfactory elemental analyses were obtained.