A Novel Cleavage of Five-Membered Cyclic Acetals Using Sodium Hydrogen Telluride

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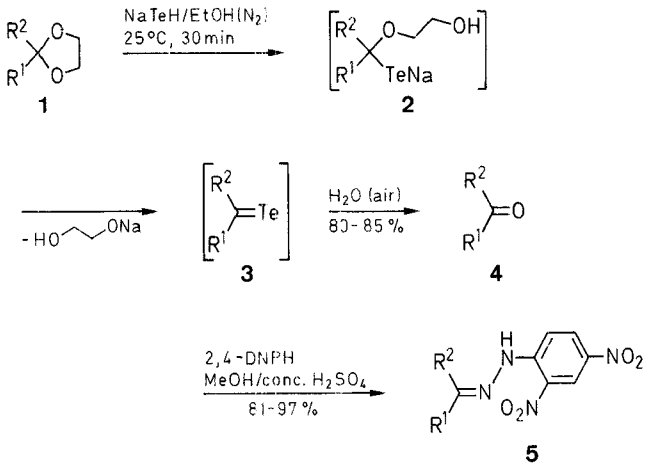
Under mild conditions, a variety of 1,3-dioxolanes are easily cleaved in high yields by treatment with sodium hydrogen telluride in ethanol.

Sodium hydrogen telluride (NaTeH) is a versatile reagent of increasing interest. It has found various applications in organic synthesis,[1] particularly in debromination,[2-3] in reductions of nitro groups[4-5] and α,β-unsaturated carbonyl compounds,[6] and in the synthesis of benzyl ethers.[7] We have described further uses of sodium hydrogen telluride in the cleavage of carboxylic esters[8] and 2-haloethyl esters,[9] and in the reductions of imines[10] and α-diketones.[11] We now report the successful application of this reagent to the deprotection of acetals.



1–5	R^1	R^2	1–5	R^1	R^2
a	*n*-Pr	H	g	$(CH_2)_5$	
b	*i*-Bu	H	h	$(CH_2)_6$	
c	Ph	CH_3	i	Ph	H
d	*n*-Pr	CH_3	j	4-$CH_3C_6H_4$	H
e	Ph	Ph	k	Ph	CH_3
f	*i*-Bu	CH_3	l	Ph	Et

In general, the hydrolysis of acetals is effected under acidic conditions to give the appropriate aldehydes and ketones.[12] Wet silica gel,[13] mercuric ion,[14] and activated zinc dust[15] have also been used for deacetalization and recently, a mild basic two-step cleavage of acetals using 2-(2-pyridyl)propane-1,3-diol was reported,[16] but its applicability is restricted. With our new method, however, acetals are readily cleaved under mild basic conditions in one step. Thus, aldehydes and ketones are released from 1,3-dioxolanes (prepared by acetalization of the carbonyl compounds with ethylene glycol) in high yields by treatment with sodium hydrogen telluride, which is easily prepared from tellurium powder and sodium borohydride in ethanol.[17] The cleavage of 1,3-dioxolanes **1** was performed at room temperature in a one-pot procedure. The proposed mechanism proceeds via **2** and **3** as intermediates, which are hydrolyzed. The aldehydes and ketones **4** thus obtained were isolated by distillation or converted into the 2,4-dinitrophenylhydrazones **5** which were characterized by their melting points and ^{1}H-NMR spectra. The sodium hydrogen telluride is reconverted into tellurium powder during the reaction, and may be easily removed by filtration. The results shown in the Table demonstrate that a wide range of acetals, both aliphatic and aromatic, may be cleaved in this manner. Besides the simplicity of the procedure, the easy isolation, and the high yields, the main advantages of this novel method are the mild basic conditions and utilization of the easily available sodium hydrogen telluride.

Conversion of 1,2-Ethanediyl Acetals of Aldehydes and Ketones (1, 1,3-Dioxolanes) into 2,4-Dinitrophenylhydrazones 5; General Procedure:
EtOH (20 mL) is added to a mixture of Te powder (1.27 g, 10 mmol) and $NaBH_4$ (0.90 g, 24 mmol) under N_2. This mixture is stirred and refluxed until the Te powder has been completely consumed and no further gas is evolved (1.5 h). The mixture is allowed to cool to r.t., the 1,3-dioxolane **1**[19] (5 mmol) is added, and stirring is continued at 25 °C for 30 min. The excess NaTeH is destroyed by the addition of H_2O (10 mL) and the Te powder produced during the reaction and by hydrolysis of the excess NaTeH is filtered off. 2,4-Dinitrophenylhydrazine (2,4-DNPH; 1.5 g, 7.5 mmol) in aq. MeOH (30 mL) and conc. H_2SO_4 (4 mL) are added to the filtrate at 25 °C, filtration of the resulting precipitate gives the derivate **5**, which is purified and characterized as shown in the Table. Under similar conditions, no precipitate is formed when 2,4-dinitrophenylhydrazine is added directly to 1,3-dioxolane without previous treatment with NaTeH.

Isolation of Carbonyl Compounds 4; General Procedure:
After the Te powder is filtered off as described above, the aqueous ethanol solution is extracted with Et_2O (3 × 25 mL), the organic phase is dried ($MgSO_4$). Removal of the solvent and distillation gave the carbonyl compound **4**.

Table. 2,4-Dinitrophenylhydrazones **5** from 1,2-Ethanediyl Acetals **1**

Product	Yield (%)	mp (°C) found	mp (°C) Lit.[18]	^{1}H-NMR[a] (DMSO-d_6/TMS) δ, *J* (Hz)
5a	85	118–120	122	11.3 (s, 1H); 7.75–8.86 (m, 3H); 8.00 (m, 1H); 2.16–2.50 (m, 2H); 1.33–1.75 (m, 2H); 1.00 (t, 3H, *J* = 6)
5b	83	120–122	123	11.35 (s, 1H); 7.75–8.86 (m, 3H); 8.06 (m, 1H); 2.14–2.30 (m, 2H); 1.30–2.03 (m, 1H); 1.03 (d, 6H, *J* = 6)
5c	91	111–113	115	10.80 (s, 1H); 7.75–8.86 (m, 3H); 2.50 (q, 2H, *J* = 7); 2.06 (s, 3H); 1.20 (t, 3H, *J* = 7)
5d	94	140–143	144	10.82 (s, 1H); 7.80–8.90 (m, 3H); 2.30–2.50 (m, 2H); 2.15 (s, 3H); 1.40–1.80 (m, 2H); 1.00 (t, 3H, *J* = 7)
5e	93	153–154	155	11.0 (s, 1H); 7.80–8.90 (m, 3H); 2.50 (q, 4H, *J* = 7); 1.20 (t, 6H, *J* = 7)
5f	93	92–94	95	10.15 (s, 1H); 7.70–8.84 (m, 3H); 2.05–2.50 (m, 3H); 2.00 (s, 3H); 0.90 (d, 6H, *J* = 6)
5g	90	159–161	162	11.0 (s, 1H); 7.75–8.90 (m, 3H); 1.55–2.50 (m, 10H)
5h	81	147–148	148	10.85 (s, 1H); 7.75–8.90 (m, 3H); 1.60–2.60 (m, 12H)
5i	97	229–230	235	10.00 (s, 1H); 7.50–8.95 (m, 9H)
5j	93	234–236	234	10.20 (s, 1H); 7.25–8.95 (m, 8H); 2.40 (s, 3H)
5k	97	236–237	237	10.05 (s, 1H); 7.40–8.90 (m, 8H); 1.75 (s, 3H)[b]
5l	96	187–189	191	10.0 (m, 1H); 7.50–8.90 (m, 8H); 2.95 (q, 2H, *J* = 7); 1.30 (t, 3H, *J* = 7)

[a] Recorded on a JEOL JUM-PMX 60 SI spectrometer.
[b] Recorded on a JEOL FX 90Q spectrometer.

4l: oil; bp 216–218 °C; yield: 85%.

^{1}H-NMR ($CDCl_3$): δ = 8.20–7.30 (m, 5 H); 3.00 (q, 2 H, J = 7); 1.35 (t, 3 H, J = 7).

4k: oil; bp 200–202 °C; yield: 80%.

^{1}H-NMR ($CDCl_3$): δ = 8.20–7.30 (m, 5 H); 2.20 (s, 3 H).

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