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Reductive Telluration of Aliphatic Aldehydes with Hydrogen Telluride. A New Synthesis of Dialkyl Ditellurides

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Reaction of aliphatic aldehydes with hydrogen telluride under acidic conditions gave dialkyl ditellurides in moderate yields. The use of deuterium telluride formed in situ from aluminum telluride and deuterium oxide provided a facile synthetic method of 1,1'-dideuterated dialkyl ditellurides.

During the course of our study on the reduction using hydrogen telluride (H_2Te) as a reducing agent, we have found that hydrogen telluride has a unique reducing ability toward a variety of functional groups such as activated double bonds, carbonyls, and some nitrogen containing functional groups giving rise to corresponding hydrogenated compounds.[1,2] We report here that under acidic conditions the reaction of aliphatic aldehydes with hydrogen telluride proceeds in a different manner leading to dialkyl ditellurides.

In the above hydrogenative reduction of carbonyl compounds, aliphatic aldehydes and ketones gave relatively poor yields of corresponding alcohols and the reduction was always accompanied by formation of dialkyl ditellurides(Eq. 1). In order to obtain the ditelluride as the major product, we examined the reaction conditions and found that aliphatic aldehydes gave corresponding ditellurides in moderate yields when acidic conditions were employed. As shown in Table 1, the

$$\mathrm{RCHO} \xrightarrow[\mathrm{THF}]{\mathrm{Al_2Te_3,\ H_2O}} \mathrm{RCH_2OH} + (\mathrm{RCH_2Te})_2 \qquad (1)$$

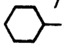
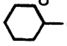
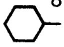
Table 1. Reaction of Octanal with Hydrogen Telluride[a)]

Additive	$(n\text{-}C_8H_{17}Te)_2$ Yield / %[b)]	$n\text{-}C_8H_{17}OH$ Yield / %[b)]	$n\text{-}C_7H_{15}CHO$ Recovered / %[b)]
none[c)]	29	41	8
CH_3COOH	13	trace	55
$CH_2ClCOOH$	8	trace	61
CF_3COOH	53	trace	5
$PhSO_3H$	54	6	19
H_2SO_4[d)]	52	5	24
Et_3N[e)]	0	65	29

a) Octanal(2 mmol), Al_2Te_3(2 mmol), H_2O(24 mmol), additive(4 mmol), THF(10 ml), 66 °C, 1.5 h.
b) Isolated yield. c) 20 h. d) H_2SO_4(2 mmol).
e) Octanal(1 mmol), 3 h.

product distribution is greatly affected by the additives used. Addition of weak acids suppressed the formation of both ditellurides and alcohols. In the presence of relatively strong acids, the ditelluride formation predominated. Under basic conditions formation of ditelluride was not observed. Some representative results obtained using sulfuric acid are shown in Table 2.[3)] Aliphatic aldehydes gave corresponding ditellurides in moderate yields. Under identical conditions benzaldehyde was reduced to benzyl alcohol exclusively. In the case of 3-phenylpropenal reduction of the C-C double bond preceded giving rise to bis(3-phenylpropyl) ditelluride(48%) together with 3-phenylpropanal(28%). The reaction of ketones was sluggish under similar conditions. For example, cyclohexanone gave dicyclohexyl ditelluride in 11% yield. In any cases, corresponding dialkyl tellurides were not formed.

Table 2. Synthesis of Dialkyl Ditellurides[a)]

Substrate	Ditelluride, Yield / %[b)]		Alcohol, Yield / %[b)]	
$n\text{-}C_7H_{15}CHO$	$(n\text{-}C_8H_{17}Te)_2$	53	$n\text{-}C_8H_{17}OH$	1
-CHO	($-CH_2Te)_2$	46	$-CH_2OH$	1
Me_3CCHO	$(Me_3CCH_2Te)_2$	56	Me_3CCH_2OH	c)
$PhCH_2CH_2CHO$	$(PhCH_2CH_2CH_2Te)_2$	53	$PhCH_2CH_2CH_2OH$	1[d)]
$PhCH_2CHO$	$(PhCH_2CH_2Te)_2$	34	$PhCH_2CH_2OH$	7[d)]
PhCHO	$(PhCH_2Te)_2$	0	$PhCH_2OH$	93
PhCH=CHCHO	$(PhCH_2CH_2CH_2Te)_2$	48	$PhCH_2CH_2CH_2OH$	2

a) Substrate(2 mmol), Al_2Te_3(4 mmol), H_2O(96 mmol), H_2SO_4(4 mmol), THF(10 ml), 66 °C, 1.5 h.
b) Isolated yield. c) Not determined. d) Glc yield.

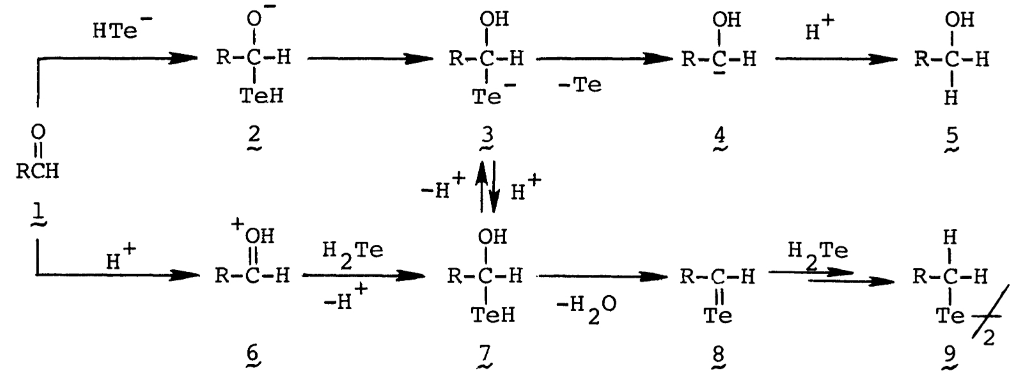
Applicability of D_2O as the deuterium source is an advantage of the present reaction. When D_2O was used in place of H_2O, 1,1'-dideuterated dialkyl ditellurides were obtained in a similar manner.³⁾ It should be noted that "protic" deuterium has been introduced as deuteride in the product.

$$\underset{(2\ \text{mmol})}{\text{RCHO}} \xrightarrow[\substack{\text{H}_2\text{SO}_4(4\ \text{mmol}),\ \text{THF}(10\ \text{ml}) \\ 66\ ^\circ\text{C},\ 1.5\ \text{h}}]{\text{Al}_2\text{Te}_3(4\ \text{mmol}),\ \text{D}_2\text{O}(96\ \text{mmol})} (\text{RCHDTe})_2 \qquad (2)$$

$R = PhCH_2CH_2$ 70%

$= t\text{-Bu}$ 56%

The effect of additives on the course selectivity of the reaction may be explained as follows.⁴⁾ Under acidic conditions, ionization of Te-H group is suppressed and equilibrium between 3 and 7 is biased to 7. The following acid catalyzed dehydration of 7 proceeds to give 8 which is then reduced to give ditellurides. Although the intermediacy of 8 has not been confirmed and alternative pathways are possible in the present reaction, similar mechanisms have been proposed in the reductive selenation of carbonyl compounds with hydrogen selenide.⁵⁻⁸⁾



Scheme 1.

Ditellurides have been usually prepared by the oxidation of metal tellurolates (RTeM, M=Li, or MgX),⁹⁾ reduction of organotellurium trichlorides($RTeCl_3$),¹⁰⁾ and alkylation of sodium ditelluride(Na_2Te_2) with alkyl halides.¹¹⁾ Present reaction could be a useful supplementary method especially for the preparation of deuterated dialkyl ditellurides.

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References

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3) A typical experimental procedure is as follows. Deuterium oxide solution of sulfuric acid(4 mmol of 98% H_2SO_4 in 96 mmol of D_2O) was added to a suspension of 3-phenylpropanal(2 mmol) and aluminum telluride(4 mmol) in THF(10 ml) at -78 °C. The mixture was heated to the reflux temperature with stirring over 30 min and refluxed for 1.5 h. After black precipitate was filtered, the filtrate was washed with aqueous sodium hydrogen carbonate and dried over calcium sulfate. Filtration of the solvent gave a crude product which was chromatographed(hexane:benzene=1:1) to give 350 mg of bis(3-phenylpropyl-1-*d*) ditelluride(dark red oil, 70%). Mass and ^{1}H-NMR spectra showed that d-content at α-position was higher than 0.90. Although deuteration of α-position of the starting aldehyde via acid catalyzed enolization may be expected, d-content at β-position of the ditelluride was negligible.

4) In the reduction using sodium hydrogen telluride(NaTeH), processes similar to the steps of **3** to **4** and **2** to **5** have been proposed; D. H. R. Barton and S. W. McCombie, J. Chem. Soc., Perkin Trans. 1, 1975, 1574; H. Suzuki and K. Takaoka, Chem. Lett., 1984, 1733; D. H. R. Barton, A. Fekih, and X. Lusinchi, Tetrahedron Lett., 26, 3693(1985).

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11) For example, see: M. T. Chen and J. W. George, J. Organomet. Chem., 12, 401(1968).

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