

Reaction of *cis*-Vicinal Dimethanesulfonates with Te^{2-} : a Method for converting *cis*-Vicinal Diols into Olefins and its Use in the Preparation of 2',3'-Didehydro-2',3'-dideoxynucleosides

Derrick L. J. Clive* and Philip L. Wickens

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

cis-Vicinal dimethanesulfonates, prepared from the corresponding diols, are converted into olefins by treatment with alkali metal tellurides or selenides (M_2Te or M_2Se); the reaction has been used to make derivatives of 2',3'-didehydro-2',3'-dideoxynucleosides.

Conversion of 1,2-diols into olefins is a useful process¹ which has attracted renewed attention because of its relevance to the synthesis of 2',3'-didehydro-2',3'-dideoxy- and 2',3'-dideoxynucleosides² needed in the palliative treatment³ of HIV infection.

We report that conversion of *cis*-1,2-diols into the corresponding dimesylates (dimethanesulfonates), followed by treatment with lithium telluride, generated *in situ* from metallic tellurium and lithium triethylborohydride (Super-Hydride),⁴ leads to olefins. Sodium telluride (Na_2Te), which is

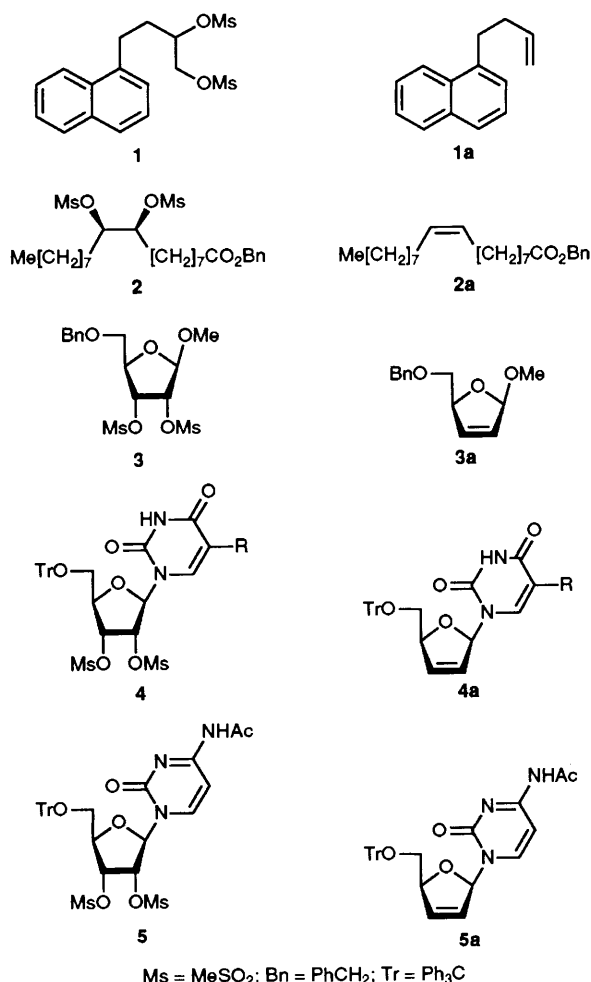
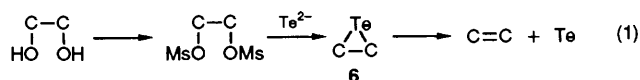


Table 1 Preparation of olefins from dimesylates using metal tellurides or selenides^a

Entry	Dimesylate	M ₂ X	Solvent	t/h	Product	Yield (%)
1	1	Li ₂ Te	A	20	1a	88
2	2	Li ₂ Te	A ^b	2	2a	83
3	2	Li ₂ Se	B ^b	4	2a	76
4	3	Li ₂ Te	B ^c	20	3a	69
5	4, R = H	Li ₂ Te	B	48	4a, R = H	80
6	4, R = H	Li ₂ Se	A	24	4a, R = H	65
7	4, R = H	Na ₂ Se	A	48	4a, R = H	51
8	4, R = H	Na ₂ Te	A	20	4a, R = H	93
9	4, R = Me	Li ₂ Te	A	48	4a, R = Me	90
10	5	Li ₂ Te	A	24	5a	ca. 71

^a All lithium salts were generated using Super-Hydride and sodium salts were prepared from sodium and tellurium (or selenium) in liquid ammonia, followed by evaporation of the ammonia. Reactions were carried out at room temperature unless otherwise noted. Solvent A = THF; B = THF-dioxane. ^b Bath temp. 100 °C. ^c Bath temp. 105 °C.



easily prepared⁵ from sodium and tellurium in liquid ammonia, may also be used, and our results are summarized in Table 1.

The reaction probably follows the pathway shown in eqn. (1). Epitellurides **6** are known to collapse spontaneously to olefins,⁶ and the proposed mechanism accounts for the observed double bond geometry (Table 1, entry 2).

Each of the dimesylates listed in Table 1 was prepared in the usual way⁷ (methanesulfonyl chloride, pyridine or triethylamine; ca. 75% for **5**, and 83–96% yield for the other examples) from the corresponding diol, and then added [ca. 0.05–0.2 mol dm⁻³ in tetrahydrofuran (THF)] to a THF suspension of lithium telluride⁴ (0.35 to 0.45 mol dm⁻³, 2.0 mmol per mmol dimesylate). The resulting mixture was stirred for the indicated time, usually at room temperature. In two cases (entries 3 and 4) the mixture was diluted with dioxane and heated. Reaction took place easily in the nucleoside series but it is not clear why the simple ribose example (entry 4) required a higher temperature.

When the reaction is done using sodium telluride under our standard conditions (see Table 1), the reagent⁵ (after evaporation of the ammonia) is suspended in THF and a solution of the dimesylate in the same solvent is added.

As episelenides also collapse spontaneously to olefins,⁸ a similar reaction should take place with lithium and sodium selenides, and this was confirmed with several examples (entries 3, 6 and 7).

Methods for removal of 5'-O-trityl and N-acyl groups are well established^{2,9} and so the preparation of compounds **4a** and **5a** constitutes a route to the corresponding deprotected nucleosides and/or their hydrogenation products.

All new compounds were fully characterized by spectroscopic measurements including mass measurement.

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