

1 Type of the Paper (Article, Review, Communication, etc.)

2 Unexpected ethyltellurenylation of epoxides with 3 elemental tellurium under lithium 4 triethylborohydride conitions

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10 Received: date; Accepted: date; Published: date

11 **Abstract:** The one-pot multistep ethyltellurenylation reaction of epoxides with elemental tellurium
12 and lithium triethylborohydride has been described. The reaction mechanism has been
13 experimentally investigated. Lithium ditelluride and triethyl borane, formed from elemental
14 tellurium and lithium triethylborohydride, were shown to be the key species involved in the
15 reaction mechanism. Epoxides undergo ring-opening reaction with lithium ditelluride to afford
16 β -hydroxy ditellurides, which are sequentially converted into the corresponding β -hydroxy-alkyl-
17 ethyltellurides by transmetalation with triethyl borane, reasonably proceeding through S_N2
18 mechanism.

19 **Keywords:** tellurium; tellurides; ditellurides; superhydride; boranes; ring-opening-reactions;
20 epoxides; transmetalation; radicals.

21

22 1. Introduction

23 Organoselenium [1,2] and organotellurium [3] compounds continue to find wide application in
24 chemical sciences and biology [4-8]. Tellurium-containing derivatives play an important role in
25 organic synthesis [3,9], materials sciences [10,11], and medicinal chemistry [8,12-15]. The
26 incorporation of tellurium atoms into organic structures is often a rewarding strategy in developing
27 new enzyme modulators [14-17], catalysts [18], smart materials [10,11], and
28 glutathione-peroxidase-like antioxidants [19-25]. Additionally, often undergoing regio- and
29 stereo-selective transformations, organotellurium compounds can be employed in synthetically
30 useful functional group conversion reactions [26,27] and carbon-carbon bond-forming
31 processes.[28-30] Owing to these features, tellurenylation reactions provide an attractive functional
32 handle for further elaboration. The development of new, reliable, and general methodologies
33 towards these chalcogen-containing organic molecules is thus highly sought after in organic
34 synthesis. Particularly, the possibility to access densely functionalised and sp^3 -rich compounds,
35 characterised by high molecular complexity, enables the possibility to define and explore new
36 chemical space and plays a key role in terms of successfully developing new catalysts and drug
37 candidates [31,32]. Furthermore, sp^3 -rich organochalcogens bearing O- and N-containing
38 functionalities have been demonstrated to possess improved catalytic and pharmacological
39 properties [15-17,20,23]. However, although a number of methods towards selenides and tellurides
40 have been reported, a number of limitations remained, including functional-group compatibility
41 and the harsh reaction conditions. Therefore, the development of mild procedures for the synthesis
42 of densely functionalised molecules still remains challenging.

43 Three-membered heterocycles such as epoxides and aziridines, often undergoing regioselective
 44 nucleophilic ring-opening reactions (NRORs), represent convenient starting materials for the
 45 synthesis of functionalised chalcogen-containing systems [33]. A number of ring-opening-based
 46 procedures towards hydroxy- and amino-substituted selenides and tellurides have been developed
 47 over the last decade [34-39]. Such a functionalised chalcogenides have also been employed as
 48 intermediates for the synthesis of valuable compounds [40,41] and as organocatalysts for the
 49 asymmetric addition of diethylzinc to aldehydes [42].

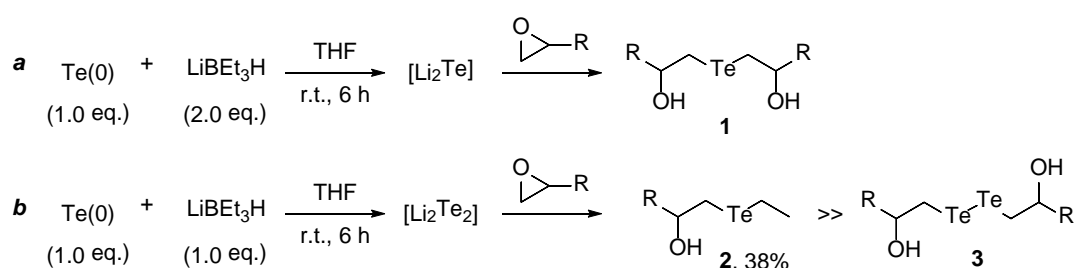
50 In this communication, as a part of our growing interest in the study of the chemistry of
 51 organotellurium compounds, we report a study on the mechanism of an unexpected reaction of
 52 epoxides with elemental tellurium and lithium triethylborohydride, leading to the formation of
 53 β -hydroxy-alkyl-ethyl-tellurides.

54 2. Results

55 During the course of our studies on the reactivity of strained heterocycles with
 56 selenium-centered nucleophiles we developed convenient routes towards a variety of hydroxy-,
 57 amino-, and mercapto-substituted Se-containing systems [43-45]. For example, through the tuning of
 58 the stoichiometry and the conditions of the reaction of $(\text{Me}_3\text{Si})_2\text{Se}$ [(bis(trimethylsilyl)selenide, a
 59 synthetic equivalent of hydrogen selenide] with epoxides, thiiranes, and aziridines, we were able to
 60 successfully achieve a range of functionalised selenols [43], selenides, and diselenides [46].

61 Attracted by the synthetic utility and versatility of organotellurium compounds, we recently
 62 moved to evaluate the chemistry of tellurium-centered nucleophiles with strained heterocycles
 63 [47,48]. The poor stability of $(\text{Me}_3\text{Si})_2\text{Te}$ [49] prompted us to employ lithium telluride and lithium
 64 ditelluride, generated from elemental tellurium and lithium triethylborohydride (superhydride), as
 65 tellurenylation reagents for the NRORs of epoxides and aziridines [48]. However, while ring
 66 opening of epoxides with Li_2Te provided access to symmetrical β -hydroxy-tellurides **1** (Scheme 1,
 67 part a), the reaction with Li_2Te_2 gave almost exclusively ethyl-alkyl-tellurides **2** instead of the
 68 expected β -hydroxy-ditellurides **3**, which were isolated only in traces amount (Scheme 1, part b).
 69 Intrigued by this result, we wished to deeper investigate such a transformation in order to establish
 70 the mechanism involved in the formation of unsymmetrical hydroxy-ethyl-tellurides **2**.

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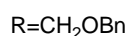
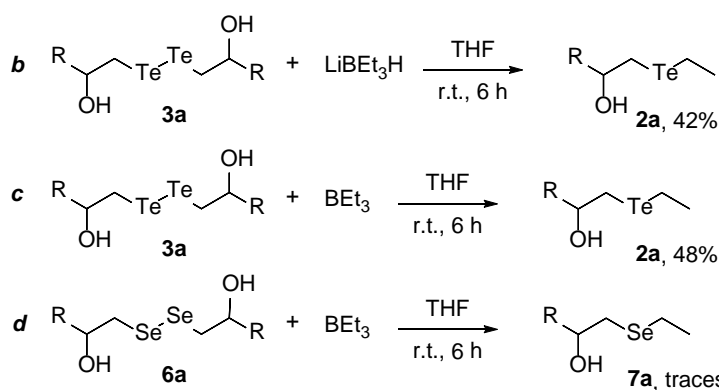
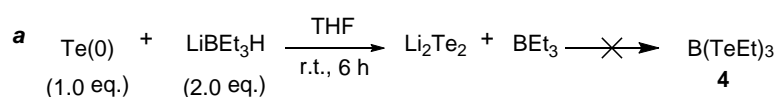
74 **Scheme 1.** Reactivity of epoxides with Li_2Te and Li_2Te_2 , generated from elemental tellurium under
 75 lithium triethylborohydride conditions. **a**, Synthesis of tellurides **1**. **b**, Unexpected formation of
 76 ethyl-alkyl-tellurides **2**.

77 A plausible explanation for the formation of unsymmetrical tellurides **2** involves the
 78 transmetalation of triethylborane with β -hydroxy-ditellurides **3**. However, an alternative path could
 79 proceed through the ring-opening of epoxides with tris(ethyltelluro)borane **4** which, in principle,
 80 could be generated from lithium ditelluride and triethyl borane. A series of control experiments
 81 were therefore undertaken in order to test these hypotheses.

82 We initially evaluated whether tris(ethyltelluro)borane **4** could be generated upon treatment of
 83 elemental tellurium with lithium triethylborohydride. However, the formation of **4** was not
 84 observed under the standard reaction conditions (Scheme 2, reaction *a*). Traces of **4** were detected
 85 neither performing the reaction in a coaxial NMR tube and monitoring its progress over the time.

86 On the basis of these results, we next turned our attention in evaluating whether under the
 87 studied conditions ditellurides **3** could behave as precursors of tellurides **2**. We recently developed
 88 an *on water* methodology to access functionalised dialkyl ditellurides from elemental tellurium,
 89 sodium hydroxymethanesulfinate, and strained heterocycles [50]. Therefore, we employed this route
 90 to prepare β -hydroxy-ditellurides and then we studied their reactivity with organoboranes.
 91 β -Hydroxy-ditelluride **3a** was thus treated with lithium triethylborohydride and, pleasingly,
 92 β -hydroxy-ethyl-alkyl-telluride **2a** was formed in 42% yield (Scheme 2, reaction *b*). However, under
 93 these conditions the alkyltelluroate **5a**, arising from the LiBEt_3H -induced reduction of the
 94 ditelluride **3a**, could be the species actually involved in the formation of **2a**. Unequivocal proof for
 95 the direct involvement of ditelluride **3a** and triethylborane was obtained by the reaction of these two
 96 compounds which, in absence of hydrides, afforded **2a** in 48% yield (Scheme 2, reaction *c*). Notably,
 97 related diselenide **6a** reacted slowly with triethylborane under the same conditions and only traces
 98 of unsymmetrical ethyl-selenide **7a** were detected after 6 h (Scheme 2, reaction *d*).

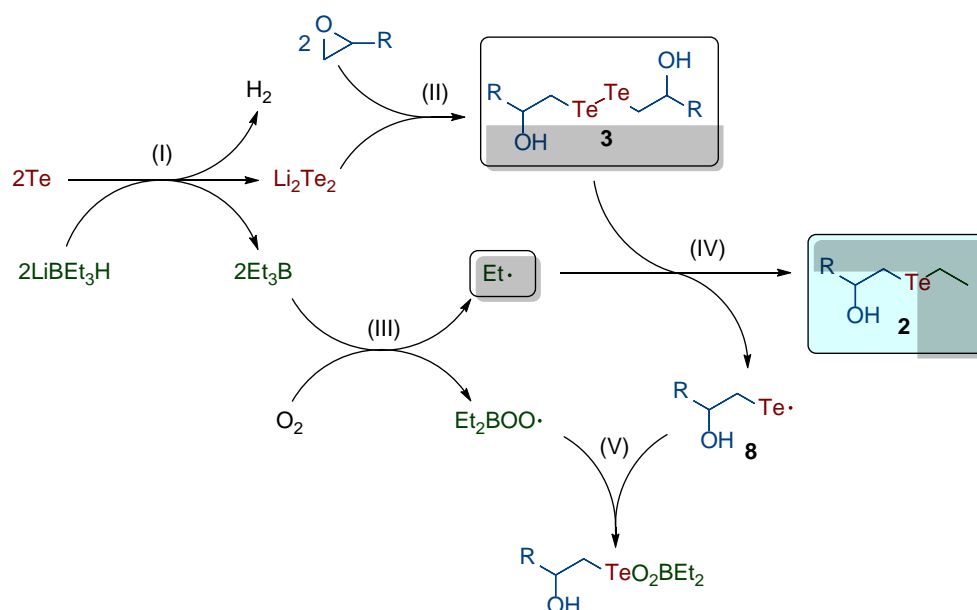
99 Trialkyl boranes readily undergo radical reactions generating alkyl radicals. Such processes can
 100 be initiated by oxygen, light or radical initiators, such as AIBN [51]. Additionally, ditellurides have
 101 been demonstrated to easily react with alkyl radicals, exhibiting remarkable radical-trapping activity
 102 [52]. On the basis of these considerations and supported by a literature precedent describing the
 103 reactivity of diphenyl ditelluride with organoboranes [53], we hypothesised a radical process
 104 involving ditellurides **3** and ethyl radicals. Control experiments performed using BHT
 105 (3,5-di-*tert*-butyl-4-hydroxytoluene) as a radical inhibitor further demonstrated a radical pathway.
 106 Additionally, performing reactions *b* and *c* (Scheme 2) in the dark had no significant effect on the
 107 reaction outcome, showing that the light was not required for the process leading to **2a**.
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 111 **Scheme 2.** Control experiments.
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113 On the basis of the control experiments and of precedent reports, a proposed reaction
 114 mechanism is reported in the Scheme 3. The first step (I) involves the reduction of elemental
 115 tellurium with lithium triethylborohydride, leading to the formation of lithium ditelluride and
 116 triethylborane. Subsequently (II), Li_2Te_2 reacts with two equivalents of epoxide to afford the
 117 corresponding ditelluride **3** through a regioselective nucleophilic ring-opening-reaction. The
 118 following transmetalation of Et_3B with **3** reasonably proceeds through the oxygen-mediated
 119 formation of ethyl radicals (III) which, in turn, react with the ditelluride **3** providing the
 120 unsymmetrical hydroxyl-ethyl-telluride **2** through an $\text{S}_{\text{H}2}$ process (IV) [54,55]. The
 121 tellurium-centered radical **8**, formed in the $\text{S}_{\text{H}2}$ reaction, undergoes typical propagation and
 122 termination processes, including the recombination with a second equivalent of **8** providing

123 ditelluride **3** [56]. Furthermore, the reaction of **8** with oxygen or borylperoxyl radicals (V) would
 124 afford reactive tellurenyl peroxides which plausibly decompose, thus explaining the rather low yield
 125 of the transmetalation reaction and the absence of ditelluride **3**, or unreacted epoxide in the crude
 126 mixture.
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Scheme 3. Proposed mechanism for the formation of unsymmetrical hydroxy-ethyltellurides **2**.

132 3. Conclusions

133 In conclusion, we have described a one-pot multistep reaction in which epoxides are converted
 134 into the corresponding unsymmetrical β -hydroxy-ethyltellurides upon treatment with elemental
 135 tellurium under lithium triethylborohydride reducing conditions. The reaction mechanism has been
 136 experimentally investigated; β -hydroxy ditellurides and triethyl borane were demonstrated to be the
 137 key species involved in this one-pot ethyltellurenylation reaction. The transmetalation of triethyl
 138 borane with hydroxy-dialkyl-ditellurides, reasonably occurring through an oxygen-induced $S_{\text{H}}2$
 139 mechanism, represents the key step of the process. The findings here described can be exploited for
 140 the development of novel general methodologies towards the synthesis of synthetically and
 141 biologically valuable complex sp^3 -rich unsymmetrical tellurides. Further studies on the application
 142 of this reaction to functionalised boranes (and boronic esters) for the preparation and the elaboration
 143 of poly-functionalised unsymmetrical tellurides are currently on-going in our laboratories.

144 4. Materials and Methods

145 4.1 Experimental Section

146 All reactions were carried out in an oven-dried glassware. Solvents were dried using a solvent
 147 purification system (Pure-SolvTM). All commercial materials were purchased from various
 148 commercial sources and used as received, without further purification. Flash column
 149 chromatography purifications were performed with Silica gel 60 (230-400 mesh). Thin layer
 150 chromatography was performed with TLC plates Silica gel 60 F₂₅₄, which was visualised under UV
 151 light, or by staining with an ethanolic acid solution of *p*-anisaldehyde followed by heating. High
 152 resolution mass spectra (HRMS) were recorded by Electrospray Ionization (ESI).

153 ¹H and ¹³C NMR spectra were recorded in CDCl₃ with Mercury 400, Bruker 400 Ultrashield, and
 154 Varian Gemini 200 spectrometers operating at 400 MHz for ¹H and 100 MHz for ¹³C. NMR signals

155 were referenced to nondeuterated residual solvent signals: 7.26 ppm for ^1H and 77.0 ppm for ^{13}C .
156 ^{125}Te NMR spectra were recorded in CDCl_3 at 126 MHz with a Bruker Ultrashield 400 Plus
157 instrument. $(\text{PhTe})_2$ was used as an external reference ($\delta = 420$ ppm). Chemical shifts (δ) are given in
158 parts per million (ppm), and coupling constants (J) are given in Hertz (Hz), rounded to the nearest
159 0.1 Hz. ^1H NMR data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d =
160 doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, bs = broad singlet, ecc.),
161 coupling constant (J), and assignment.

162 Ditelluride **3a** [50] and diselenide **6a** [46] were prepared from 2-((benzyloxy)methyl)oxirane
163 according to literature reported procedures.

164 4.2 General Procedure for the synthesis of β -hydroxy-alkyl-ethyl-tellurides **2**

165 Li_2Te_2 was generated according to literature [49] from 1.0 mL of a 1 M THF solution of LiEt_3BH
166 (1.0 mmol, 1.0 eq.) and elemental tellurium powder (128 mg, 1.0 mmol, 1.0 eq.), stirred at ambient
167 temperature under inert atmosphere (N_2) for 6 h. The dark red suspension of Li_2Te_2 in THF was
168 treated with the epoxide (1.0 mmol, 1.0 eq.) and the reaction was stirred for 6 h at ambient
169 temperature. Afterwards, the mixture was diluted with Et_2O (10 mL), filtered through a short pad of
170 celite, washed with sat. aq. NH_4Cl and then with H_2O (2×5 mL). The organic phase was dried over
171 Na_2SO_4 , filtered and evaporated under reduced pressure. The crude residue was then purified by
172 flash chromatography to yield β -hydroxy-alkyl-ethyl-tellurides **2**.

173 4.2.1 Synthesis of 1-(Benzyloxy)-3-(ethyltellanyl)propan-2-ol **2a**

174 According to the general procedure, 2-((benzyloxy)methyl)oxirane (152 μL , 1.0 mmol) and
175 elemental tellurium (128 mg, 1.0 mmol) gave after flash chromatography (Et_2O /petroleum ether 1:1)
176 **2a** as a colourless oil (61 mg, 38%). ^1H NMR (200 MHz, CDCl_3): δ (ppm) 1.60 (3H, t, $J = 7.6$ Hz, CH_3),
177 2.63 (2H, ap q, $J = 7.6$ Hz, $\text{CH}_3\text{CH}_2\text{Te}$), 2.63 (1H, bs, OH), 2.76-2.89 (2H, m, CH_2Te), 3.41-3.48 (1H, m,
178 $\text{CH}_a\text{H}_b\text{O}$), 3.59 (1H, dd, $J = 4.2, 9.6$ Hz, $\text{CH}_a\text{H}_b\text{O}$), 3.45-3.97 (1H, m, CHOH), 4.55 (2H, ap s, CH_2Ph),
179 7.26-7.40 (5H, m). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) -4.5($\text{CH}_3\text{CH}_2\text{Te}$), 7.7 (CH_2Te), 17.8, 70.6, 73.4,
180 74.3, 127.8, 127.8, 128.4, 137.9. ^{125}Te NMR (126 MHz, CDCl_3): δ (ppm) 213.6.

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182 **Conflicts of Interest:** The authors declare no conflict of interest.

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309 56. If regenerated, ditellurides **3** reasonably undergoes transmetallation with ethyl radicals affording
310 β -hydroxy-alkyl-ethyl-tellurides **2** and radicals **8**, following the proposed mechanism reported in the
311 Scheme 3.



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312