



Improved procedure for the hydrotelluration of alkynes

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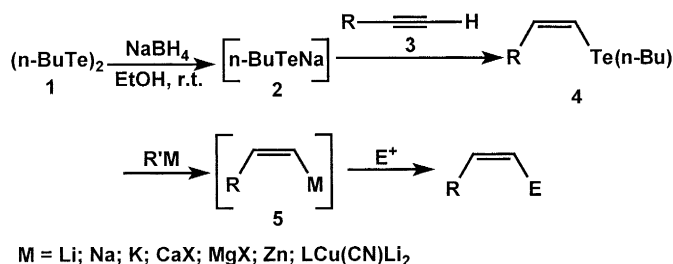
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Abstract

Z-Vinylic tellurides were prepared by hydrotelluration of alkynes with lithium butyl tellurolate generated by reaction of *n*-butyllithium with elemental tellurium. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: vinylic tellurides; hydrotelluration; lithium butyl tellurolate.

Vinylic tellurides are valuable synthetic intermediates and have recently been used in total synthesis.¹ The hydrotelluration of alkynes is the method of choice to prepare *Z*-vinylic tellurides, in view of the easy access to the starting materials,² the high regio- and stereoselectivity of the reaction and the practicality of the experimental procedure. The organo tellurolate **2** is generated by reduction of diorgano ditellurides **1** with sodium borohydride in ethanol at room temperature, and reacts with the appropriate alkyne **3** to give the vinylic telluride of the *Z* configuration **4** in good yields.³ As *Z*-vinylic tellurides **4** are used to generate *Z*-vinyloorganometallics **5** by transmetalation,³ an alkyl group, usually *n*-butyl, has to be linked to tellurium to avoid the formation of mixture of products in the transmetalation step (Scheme 1).

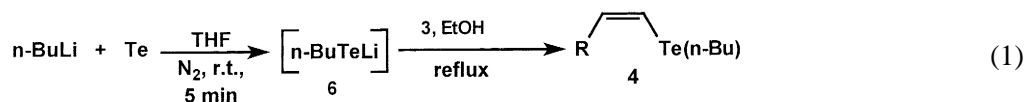


Scheme 1.

The use of dibutyl ditelluride **1** to generate the butyl tellurolate anion **2** constitutes a limitation of this methodology, since dibutyl ditelluride is not commercially available. In addition, this reagent is not stable for long periods of time, and has a very unpleasant smell, which impregnates skin and clothes. In this communication we report a practical and safe method to perform the hydrotelluration of alkynes, which avoids the use of dibutyl ditelluride.

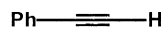
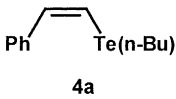

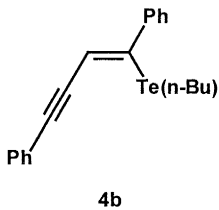
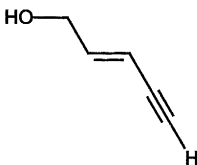
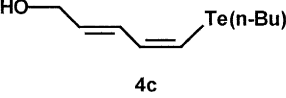
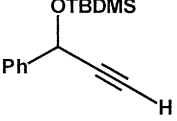
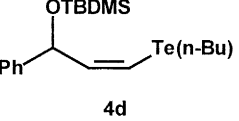
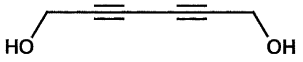
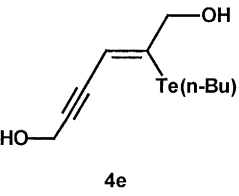
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Reaction of *n*-butyllithium with elemental tellurium in THF at room temperature under nitrogen gives lithium butyl telluroate **6**, as indicated by the consumption of the gray tellurium powder and formation of a yellow solution. To this solution is added the appropriate alkyne **3** in deoxygenated dry ethanol. Then the mixture is heated under reflux until the consumption of the alkyne, monitoring the reaction by TLC (Eq. (1)).⁴



The *Z*-vinylic tellurides **4** are obtained in yields similar to those observed in the hydrotelluration reaction using the dibutyl ditelluride/ NaBH_4 method,^{3a,5} as shown in Table 1. These vinylic tellurides are stable enough to be purified by column chromatography on a laboratory bench, and are no more unpleasant to handle than many standard reagents found in organic chemistry laboratories. Some of them

Table 1
Vinylic tellurides prepared

Entry	Alkyne	Product	Reaction Time (h)	Yield (%)
1			4	88
2			8	75
3			6	77
4			8	72
5			7	80

* Reaction performed in a 40 mmol scale.

are almost odorless. With the improvement described in this communication, the hydrotelluration of alkynes becomes a routine practice, and can be performed with no need for special safety precautions. This should stimulate the synthetic organic chemists to include *Z*-vinylic tellurides in their synthetic plans.

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References

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4. Typical procedure for the hydrotelluration with *n*-BuLi/Te: *n*-BuLi (0.66 mL, 1 mmol of a 1.5 M solution in hexane) is added dropwise to a stirred suspension of elemental tellurium (0.127 g, 1 mmol) in THF (5 mL) at room temperature under N₂. A clear solution is formed after 5 min of stirring. Then phenylacetylene (0.122 g, 1.2 mmol) in deoxygenated ethanol (10 mL) is added and the solution is refluxed for 4 h, monitoring by TLC. After this time the mixture is diluted with ethyl acetate (20 mL) and washed with brine (2×20 mL). The organic layer is separated, dried (MgSO₄) and the solvent is evaporated. The residue is purified by silica gel column chromatography eluting with hexane to give 0.215 g (75%) of the vinylic telluride **4a**.^{3a} When the reaction is performed in a 40 mmol scale, the yield rises to 88%.
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