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Synthesis of functionalized tri- and tetrasubstituted vinylic tellurides from enolphosphates through vinylic substitution by lithium butyltellurolate †

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Abstract

Vinylic tellurides are precursors of important highly reactive vinylic organometallics (e.g. vinyl Li and Cu species). Herein we report that tri- and tetrasubstituted functionalized vinylic tellurides can be prepared from enolphosphates through a vinylic substitution by lithium butyltellurolate. Starting from mixtures of *Z*- and *E*-enolphosphates, only the *Z*-vinylic telluride is formed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: vinylic tellurides; enolphosphates.

The discovery that vinylic tellurides are easily transmetallated[1] with total retention of the configuration of the double bond transformed these organoelement compounds into important intermediates for synthetic purposes.[2] In the last ten years we and others have transformed *Z*-vinylic tellurides into several reactive organometallics, namely RLi, RNa, RCaX, RMgX, $RLCu(CN)Li_2$, and RZnCl.[2]

The obtained intermediates allowed the introduction of *Z*-vinylic moieties into organic substrates by reaction with enones,[3] epoxides,[3] haloalkynes[4] and vinyltriflates.[5] In addition, *Z*-vinylic tellurides couple efficiently with organocuprates leading to olefins with the *Z*-configuration.[6] More recently we developed a catalytic coupling process involving *Z*-vinylic tellurides and alkynes promoted by $PdCl_2$/CuI giving rise to *Z*-enynes and *Z*-enediynes.[7] The singularity of these transformations lies in the *anti* hydrotelluration of alkynes, leading to *Z*-olefins in contrast to all other hydrometallation reactions of alkynes with synthetic value, which are *syn*, leading to *E*-vinylic organometallics.[8] The hydrotelluration of alkynes constitutes to date the most general method to prepare vinylic tellurides.[1b,2] However, except for the *Z*-enediynes, only disubstituted vinylic tellurides can be prepared by this method. In this communication, we report a new and very promising method for the preparation of tri- and tetrasubstituted vinylic tellurides using easily available β-dicarbonyl compounds as starting materials.

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† This paper is dedicated to Professor Nicola Petragnani on the occasion of his 70th birthday.

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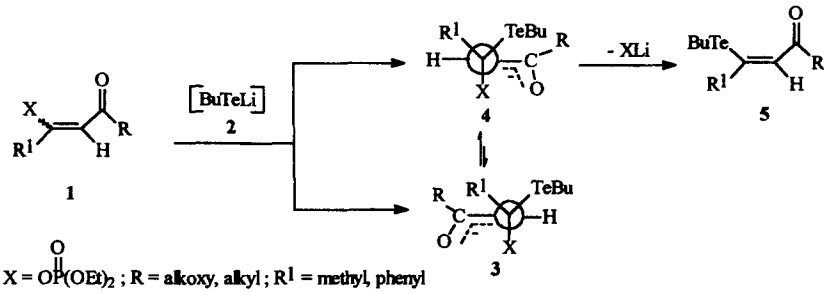
Enolphosphates of β-dicarbonyl compounds **1**[9] were added at 0°C to a solution of lithium butyltellurolate **2**, prepared by reaction of tellurium powder with *n*-butyllithium in THF at room temperature. Vinylic tellurides **5** were formed in good yields (Scheme 1, Table 1).[10]



Scheme 1.

The reaction is very fast. Analysis of the product showed that only the *Z* isomer of the vinylic telluride **5** was formed. The stereochemistry was determined by NOEDS experiments. Irradiation of the signal at 7.19 ppm, attributed to the vinylic proton of compound **5a** (Table 1), caused a signal enhancement of the signal at 2.44 ppm attributed to the CH_3 group, indicating a *cis* relationship between them. Similar experiments were performed with compounds **5b** and **5c** leading to the same conclusion. We separated the *Z* and *E* isomers of the enol phosphates **1b** and **1c** by silica gel column chromatography and reacted the pure *Z* and *E* isomers with lithium butyltellurolate **2** as described before. The reactions with the different isomers led to the same product, which was identical to the one obtained when the reaction was performed with the mixture of the *Z*- and *E*-enolphosphates. A possible explanation to this fact is that the substitution reaction occurs via an addition–elimination process.[11] The through space interaction of the carbonyl oxygen with the tellurium atom[12] should favor rotamer **4** which eliminates phosphate to give the *Z* isomer (Scheme 1).

Another approach to the synthesis of vinylic tellurides via enolphosphates developed by us consisted of the 1,4-addition of a higher order *Z*-vinylcyanocuprate (derived from the corresponding *Z*-vinylic telluride)[3] to methyl-6-oxo-1-cyclohexene-1-carboxylate and *O*-functionalization of the intermediate with diethylphosphorochloridrate leading to enol phosphate **1f**,[13] followed by substitution with lithium butyltellurolate **2** to give **5f**.

In conclusion, we have developed a versatile method for preparing tri- and tetrasubstituted vinylic tellurides from enolphosphates prepared from easily accessible β-dicarbonyl compounds. The reaction occurs under very mild conditions and gives the *Z* isomer exclusively and could be applied to the synthesis of polyunsaturated natural products[14] using tellurium chemistry.

Acknowledgements

The authors thank FAPESP and CNPq, for financial support.

References

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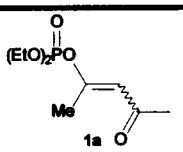
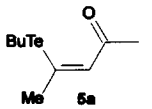
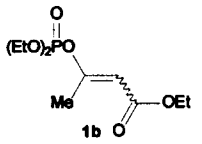
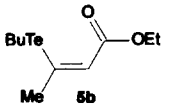
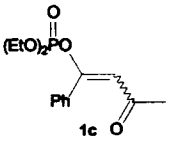
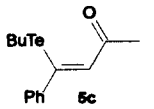
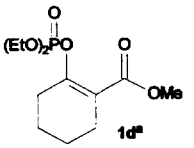
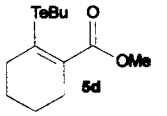
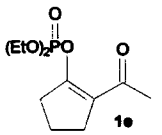
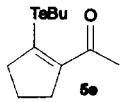
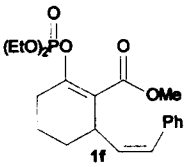
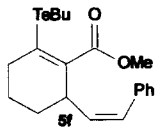
Table 1
Vinylic tellurides prepared

Entry	Enol phosphate	Telluride	Reaction time (min)	Yield[b,c] (%)
1	 8:1 (Z:E)[a]		10	85
2	 6:1 (Z:E)[a]		10	75
3	 15:1(Z:E)[a]		15	80
4			20	75
5	 87:7 (endo:exo)[a]		15	65
6			30	80

[a] used without any purification; [b] yields of the isolated products; [c] all compounds presented analytical data in accordance with the proposed structures.

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10. General procedure for the preparation of vinylic tellurides from enolphosphates: To a suspension of tellurium powder (200 mesh, 0.254 g, 2.0 mmol) in THF (2 mL) at room temperature was added *n*-BuLi (1.4 M in hexanes, 0.7 mL, 2.0 mmol). The dark mixture turned a pale yellow clear solution, which was cooled to 0°C. The appropriate enolphosphate (1.5 mmol) was then added dropwise and the reaction was monitored by TLC. Reaction times are indicated in Table 1. After the consumption of the enolphosphate ethyl acetate (20 mL) was added and the organic layer was washed with brine (3×10 mL), dried with magnesium sulphate and the solvent was evaporated. The residue was purified by silica gel column chromatography eluting with a mixture of hexane:ethyl acetate (9:1). The yields are indicated in Table 1. All compounds were isolated as yellow oils. Analytical data for compound **5b**: 500 MHz ^{1}H NMR ($CDCl_3$) δ 6.57 (q, J=1.31 Hz, 1H); 4.19 (q, J=7.1 Hz, 2H); 2.65 (t, J=7.6 Hz, 2H); 2.39 (d, J=1.3 Hz, 3H); 1.75 (quint, J=7.6 Hz, 2H); 1.43 (sext, J=7.6 Hz, 2H); 1.28 (t, J=7.1 Hz, 3H); 0.93 (t, J=7.6 Hz, 3H); 125 MHz ^{13}C NMR ($CDCl_3$) δ 168.1; 147.7; 120.9; 60.3; 33.6; 27.3; 25.3; 14.4; 13.5; 5.7; LRMS *m/z* (rel. int.) 300(20), 243(84), 215(100), 169(10), 128(12), 85(26); IR ν (cm^{-1}) 2958, 2957, 1682, 1577, 1318, 1191, 1046, 832. Anal. calcd for $C_{10}H_{18}O_2Te$: C 40.33; H 6.09. Found: C 40.23; H 5.90.
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13. Experimental procedure: To a solution of dilithium *Z*-styryl methylcyano cuprate (1.0 mmol), prepared as described in Ref. 3, cooled to −75°C was added dropwise methyl-6-oxo-1-cyclohexene-1-carboxylate (0.17 mL, 1.1 mmol). After 20 min, TMEDA (0.7 mL, 6.0 mmol) and diethylphosphorochloridrate (0.18 mL, 1.3 mmol) in THF (5 mL) were added and the solution was allowed to warm to 0°C. The reaction mixture was stirred for 1 h and then ethyl acetate (20 mL) was added. The organic phase was washed with 1:1 solution of saturated aqueous NH_4Cl and NH_4OH (3×20 mL), dried over $MgSO_4$, evaporated and the residue was purified by flash column silica gel chromatography using a 1:1 hexane:ethyl acetate mixture as eluent. Yield of **1f**: 0.30 g (70%).
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