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Highly Unsaturated Conjugated Systems from Vinylic Tellurides

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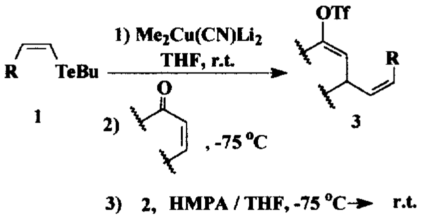
Abstract: 1,4 addition of higher order Z̲ vinyl cuprates to enones followed by triflate trapping results in the corresponding enol triflates, which can be coupled with terminal alkynes or with Z̲ vinyl zinc chloride under Pd^0 catalysis.

Keywords: Vinylic tellurides; enol triflates; cross coupling; vinyl zinc chloride.

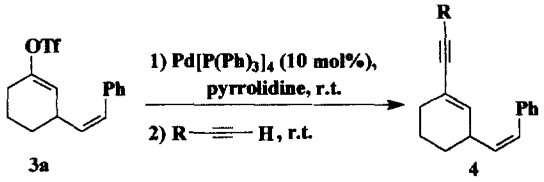
Z̲-Vinyl butyl tellurides obtained by hydrotelluration of alkynes are easily transmetallated to widely used reactive vinylic organometallics such as Z̲-vinyllithiums[1] and higher order Z̲ vinyl cyanocuprates[2]. The latter reagents has been previuosly used by us in the synthesis of Z̲-enediynes[3] and as key intermediates in the synthesis of Macrolactins[4], polyunsaturated macrolactones with anti-viral activity[5]. The success of our methodology in building unsaturated skeletons containing Z̲ double bonds and our continuous interest in the synthesis of natural products containing highly unsaturated conjugated systems led us to explore further the hydrotelluration of alkynes/transmetallation reaction of butyl vinyl tellurides **1**.

In this communication we describe the reaction of higher order Z̲-vinyl cyanocuprates with enones followed by trapping of the formed enolate with N-phenyltrifluoromethanesulfonamide (**2**) to yield the corresponding enol triflates **3a-f** (**Equation 1, Table 1**)[6].



(1)

As far as we know, this is the first report of a 1,4-addition of a higher order cyanocuprate to an enone followed by triflate trapping. Enol triflates are known to offer a broad spectrum of synthetic applications[7]. Among the synthetically interesting reactions of enol triflates are the coupling reaction with terminal alkynes catalyzed by Pd^0 [7] and the cross coupling reaction with organozinc halides also catalyzed by Pd^0 [7]. We performed the coupling of enol triflate **3a** with representative terminal alkynes under Pd[P(Ph)$_3$]$_4$ catalysis obtaining the coupled products **4** in good yields[8] (**Equation 2**).

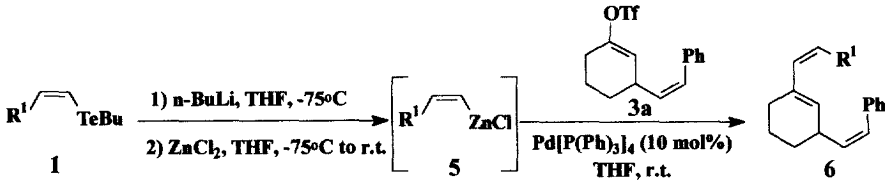


(2)

	reaction time (min)	Yield (%)
R = a) Ph	30	75
b) CH$_2$OH	20	80
c) n-Bu	45	75

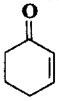
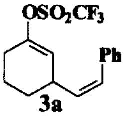
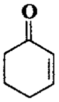
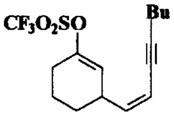
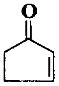
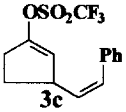
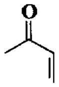
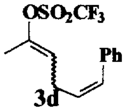
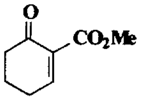
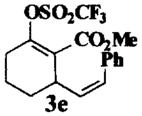
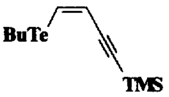
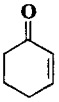
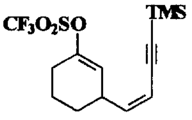
Our methodology to generate Z-vinyllithiums from Z vinyl butyl tellurides is potentially useful for the preparation of other vinylic organometallic species by reaction with the appropriate inorganic salts. In this way, lower order vinyl cyanocuprates were prepared by transmetallation of vinyl butyl tellurides with *n*-butyllithium followed by reaction with copper cyanide[9]. Analogously, we prepared vinyl zinc reagents **5** as shown in **Scheme 1**. These intermediates coupled efficiently with enol triflate **3a** under Pd[P(Ph)$_3$]$_4$ catalysis[10], generating highly unsaturated systems **6** containing two Z olefinic moieties derived from Z-vinyl butyl tellurides. In addition, some of these systems are functionalized allowing for further chain elongation through carbon-carbon bond formation.

Scheme 1



	reaction time (h)	Yield (%)
R^1 = a-) Ph	10	75
b-) Me$_3$Si—≡—	12	80
c-) n-Bu—≡—	24	75

Table 1

Telluride	Enone	Enol Triflate	Yield (%)
		 **3a**	60
		 **3b**	55
		 **3c**	50
		 **3d**	50
		 **3e**	60
 11		 **3f**	65

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1. (a) Barros, S. M., Comasseto, J. V., Berriel, J., *Tetrahedron Lett.*, **1989**, 30, 7353. For reviews see: (b) Comasseto, J. V., *Reviews on Heteroatom Chemistry*, **1993**, 9, 61; (c) Comasseto, J. V., Lo, W. L., Petragnani, N., Stefani, H. A., *Synthesis*, **1997**, 4, 373.
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5. Rychnovsky, S. D., Skalitzky, D. J., Pathirana, C., Jensen, P. R., Fenical, W. J., *J. Am. Chem. Soc.*, **1992**, 114, 671.
6. **General Procedure for the 1,4 addition of higher order mixed cyanocuprates followed by O-functionalization by N-phenyltrifluoromethanesulfonamide.** Methyllithium (4.0 mmol, 1.0 M in THF/Cumene, 4.0 mL) was added to a suspension of CuCN (dried in *Abderhalden* apparatus) (2.0 mmol, 0.18 g) in THF (10 mL) at -75 °C. The reaction mixture was then stirred until a clear solution was obtained and allowed to warm to room temperature. The appropriate *Z* vinyl butyl telluride (1.0 mmol) was added and stirred for 45 min. The solution was cooled back to - 75 °C and the enone (1.1 mmol) was added. After 20 min., HMPA (6.0 mmol, 0.6 mL) and N-phenyltrifluoromethanesulfonamide (2.6 mmol, 0.6 g) in THF (5 mL) were added and the solution was allowed to warm to room temperature. The reaction mixture was stirred for 4 h and then treated with 1:1 solution of saturated aqueous NH_4Cl and NH_4OH (20 mL), extracted with ethyl acetate (3 x 20 mL), dried, evaporated and the residue was purified by flash silica gel chromatography using hexane as eluent affording the corresponding enol triflates with the yields shown in **Table 1**.
7. For a review see: Ritter, K., *Synthesis*, **1993**, 8, 735.
8. **General procedure for the cross-coupling reaction between enol triflates and terminal alkynes, catalyzed by $Pd[P(Ph)_3]_4$.** Enol triflate **3a** (1.0 mmol, 0.33 g) was added to a stirred suspension containing a mixture of $Pd[P(Ph)_3]_4$ (10.0 mol%, 0.1 mmol, 0.11 g) and pyrrolidine (2.0 mL). The mixture was stirred for 15 min. and the appropriate terminal alkyne (1.2 mmol) was then added dropwise at room temperature. The reaction was monitored by TLC until all the starting material was consumed. After this, CH_2Cl_2 (30.0 mL) was added and the organic phase was washed with brine (3 x 20.0 mL), dried, evaporated and the residue was purified by flash silica gel chromatography using hexane as eluent.
9. Comasseto, J. V., unpublished results.
10. **General procedure for the cross-coupling reaction between enol triflates and Z-vinylic zinc chloride, catalyzed by $Pd[P(Ph)_3]_4$.** Butyllithium (1.2 mmol, 2,5 M in hexane, 0.4 mL) was added to a solution of the appropriate *Z* vinyl butyl telluride (1.2 mmol) in THF (5.0 mL) at -75 °C and stirred for 45 min. After this time, $ZnCl_2$ (1.2 mmol, 1.0 M in THF, 1.2 mL) was added and the mixture was warmed up to room temperature. This solution was transferred *via* cannula to a previously prepared mixture of $Pd[P(Ph)_3]_4$ (10.0 mol%, 0,1 mmol, 0,115 g) and the enol triflate **3a** (1.0 mmol, 0.33 g) in THF (5.0 mL). The reaction was monitored by TLC until all the starting material was consumed. After this, CH_2Cl_2 (30.0 mL) was added and the organic phase was washed with brine (3 x 20.0 mL), dried, evaporated and the residue was purified by flash silica gel chromatography using hexane as eluent.
11. Intermediate in the synthesis of a polyunsaturated antifungal agent. Ellensohn, R. M., PhD project, Instituto de Química, USP, São Paulo.