

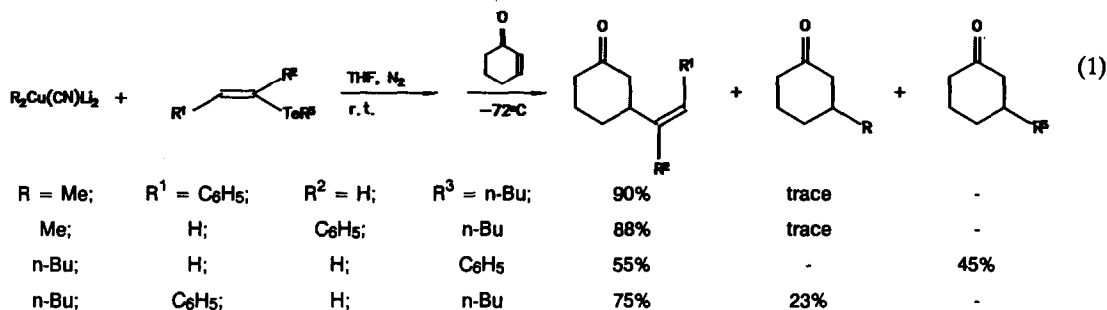
Higher Order Vinyl Cyanocuprates from Vinylic Tellurides

Fábio C. Tucci, André Chieffi and João V. Comasseto*
 Instituto de Química, Universidade de São Paulo, São Paulo-SP, Brasil

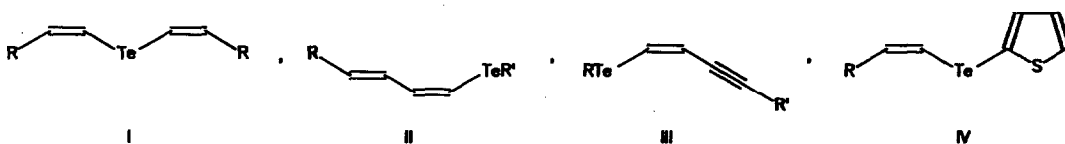
Key Words: Bis-vinylic Tellurides; Tellurodienes; Telluroenynes; Vinyl Thienyl Tellurides; Vinyl Cyanocuprates

Abstract: Bis-vinylic tellurides, 1-tellurodienes, 1-telluroenynes and vinyl thienyl tellurides react with higher order cyanocuprates giving the corresponding higher order vinyl cyanocuprates with retention of the olefine geometry.

Among the most promising synthetic applications of organic tellurium compounds are their transmetalation reactions with *n*-butyllithium¹. Recently we reported our results on the transmetalation reaction of vinylic tellurides with *n*-butyllithium leading to vinylolithium reagents^{2,3}. As an extension of this reaction we investigated a novel route to higher order mixed vinyl cyanocuprates by direct reaction between vinylic tellurides and dialkyl cyanocuprates⁴. Equation 1 summarizes the principal features of this reaction.

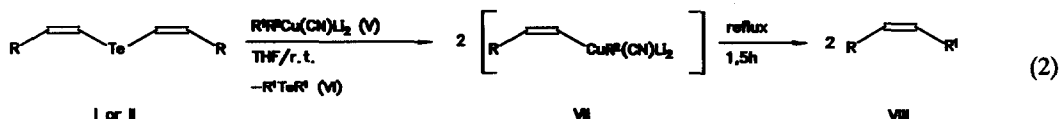


In the present communication we report on the transmetalation reaction of higher order cyanocuprates⁵ with bis-vinyl tellurides I⁶, tellurodienes II⁶, telluroenynes III³ and vinyl thienyl tellurides IV, a novel class of vinylic tellurides. In all cases the stereochemistry of the telluride double bond was *Z*.



The reaction of the vinyl cuprates derived from bis-vinyl tellurides showed to be sensitive to steric factors giving low yields of 1,4 addition with β,β disubstituted enones. In addition, in the reaction with mesityl oxide, besides the 1,4 addition products, the formation of 1-phenyl,hexa-1-ene (VIII) was observed when (*n*-Bu)₂Cu(CN)Li₂ (Va) and I (R = C₆H₅) were used. When the product of transmetalation reaction was refluxed in the absence of the enone, the olefine VIII was obtained with retention of the *Z* configuration in reasonable yields (Eq.2). Olefines resulting from reduction of the tellurium-carbon bond were formed as byproducts. Reaction with unhindered enones led to only minute amounts of the olefine VIII, the main products being the 1,4 addition of the vinyl or the butyl groups to the enone. Apparently VIII could be formed through a reductive

elimination of the intermediate vinyl cuprate **VII**. However, even using (n-Bu)(2-Th)Cu(CN)Li₂ (**Vb**) in the transmetalation reaction, the olefine **VIII** was formed. This fact suggested that the olefine **VIII** could be formed by reaction of cuprate **VII** with the byproduct dibutyltelluride (**VI**) (Eq.2). A considerable amount of styrene (17%) was observed by GLC of the crude product of this reaction.



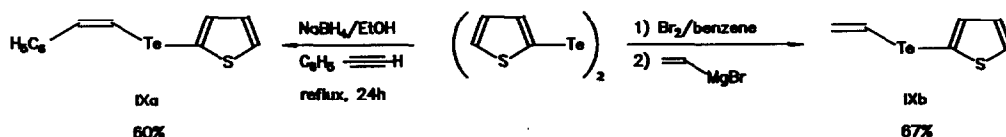
Va R¹=R²=n-Bu; R=C₆H₅ (69%); p-CH₃C₆H₄ (50%); p-ClC₆H₄ (67%); Morpholino-CH₂ (46%); THPO-CH₂-CH=CCH₃ (50%)
 Vb R¹=n-Bu; R²=2-Th; R=C₆H₅ (34%)

The fact that (n-Bu)(2-Th)Cu(CN)Li₂ (**Vb**) is efficient in promoting the transmetalation and avoids the formation of byproducts resulting from the n-butyl transfer to the enone, led us to use it instead of (n-Bu)₂Cu(CN)Li₂ (**Va**). Using the cuprate **Vb**, the transmetalation occurs rapidly with tellurides **I**. Addition of unhindered enones to the resulting mixed cuprates **VII** led to the corresponding 1,4 addition products in good yields with retention of the olefine geometry⁸. In some cases (Me)₂Cu(CN)Li₂ (**Vc**) was used in the transmetalation reactions and showed high selectivity for the transfer of the vinyl moiety (Eq.3, Tables 1 and 2).

The main advantage of using bis-vinyl tellurides **I** instead of butyl vinyl or phenyl vinyl tellurides⁴ in the transmetalation reaction with higher order cyanocuprates, is that only one equivalent of the telluride **I** is required to react with 2 equivalents of the cyanocuprate **V** generating 2 equivalents of the mixed vinylic cyanocuprate **VII**. The formation of a mixture of products observed in the reaction with non-symmetrical vinylic tellurides is also avoided (see equation 1).

A new class of vinylic tellurides (**IX**) was developed in this work. These compounds contain the vinyl and the 2-thienyl groups, the latter being a non transferable group from copper, after the transmetalation step. The vinyl thienyl tellurides **IX** were prepared by two methods: reaction of vinyl magnesium bromide with thienyl tellurenyl bromide¹⁰ and addition of thienyltellurolate to phenylacetylene (Scheme 1)⁶.

Scheme 1

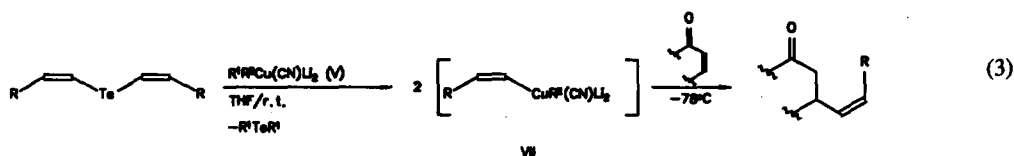


The vinyl thienyl tellurides **IX** were reacted with (n-Bu)₂Cu(CN)Li₂ (**Va**) generating in a single step the mixed cuprates **VII** which were trapped with 2-cyclohexen-1-one to give the 1,4 addition products with retention of the olefine geometry (Eq.4, Table 2)¹¹.

Tellurodienes (**II**) and telluroenynes (**III**) were also transmetalated with higher order cyanocuprates (**Vb** and **Vc**) giving the respective dienyl and enynyl mixed cuprates with retention of the double bond configuration (Table 2).

In conclusion, each equivalent of a bis-vinylic telluride is an efficient source of two equivalents of the corresponding higher order vinyl cyanocuprate. The cyanocuprate of choice for such transformation is (n-Bu)(2-Th)Cu(CN)Li₂ (**Vb**) in view of its easy access⁵ and selectivity of the posterior vinyl transfer to the enone. The ability of tellurodienes (**II**) and telluroenynes (**III**) to transmetalate with higher order cyanocuprates with retention of the olefine geometry opens a perspective for the use of these systems as intermediates in the synthesis of some classes of natural products.

Table 1

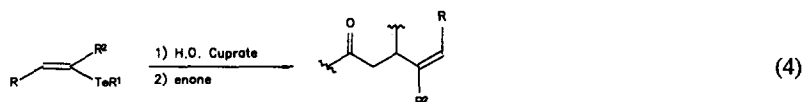


Va $R^1 = R^2 = n\text{-Bu}$; Vb $R^1 = n\text{-Bu}$, $R^2 = 2\text{-Th}$; Vc $R^1 = R^2 = \text{Me}$

R^0	H. O. Cuprate	Enone	Yield ^{a,b} (%)	R^0	H. O. Cuprate	Enone	Yield ^{a,b} (%)
1. Phenyl	Vb	Methyl Vinyl Ketone	77	9. N-methyl-morpholino	Vb	2-Cyclohexen-1-one	76
2. p-tolyl	Vb	Methyl Vinyl Ketone	69	10. N-methyl-morpholino	Vc ^d	2-Cyclohexen-1-one	82
3. p-Cl-phenyl	Vb	Methyl Vinyl Ketone	65	11. Phenyl	Vb	4,4-Dimethyl-2-cyclohexen-1-one	65
4. Phenyl	Vb ^c	2-Cyclohexen-1-one	68	12. Phenyl	Vc ^d	4,4-Dimethyl-2-cyclohexen-1-one	70
5. Phenyl	Vc ^d	2-Cyclohexen-1-one	90	13. p-Cl-phenyl	Vb	4,4-Dimethyl-2-cyclohexen-1-one	71
6. p-tolyl	Vb	2-Cyclohexen-1-one	70	14. H	Vb	4,4-Dimethyl-2-cyclohexen-1-one	75
7. p-Cl-phenyl	Vb	2-Cyclohexen-1-one	66	15. N-methyl-morpholino	Vb	4,4-Dimethyl-2-cyclohexen-1-one	54
8. H	Vb	2-Cyclohexen-1-one	78	16. N-methyl-morpholino	Vc ^d	4,4-Dimethyl-2-cyclohexen-1-one	60

a. isolated yield after column chromatography; b. The products exhibited spectral data in accordance with the proposed structures; c. When the reaction was performed in a 10mmol scale the isolated yield was 82%; d. The methyl lithium used to prepare the cuprate Vc was obtained by reacting MeI with lithium wire in diethyl ether⁹; e. The bis-vinyl tellurides were prepared as described in reference 6.

Table 2



R	R^1	R^2	H. O. Cuprate (equivalent)	Enone	Yield ^{a,b} (%)
1. H	2-Th ^d	H	Va (1.0)	2-Cyclohexen-1-one	78
2. Phenyl	2-Th ^e	H	Va (1.0)	2-Cyclohexen-1-one	82
3. THPOCH ₂ CH=CCH ₃	RCH=CR ^{2 e}	H	Vb (2.0)	Methyl Vinyl Ketone	60
4. THPOCH ₂ CH=CCH ₃	RCH=CR ^{2 e}	H	Vb (2.0)	2-Cyclohexen-1-one	78
5. C ₆ H ₅ -	n-Bu ^f	Phenyl	Vc (1.0)	2-Cyclohexen-1-one	65 ^c

a. isolated yield after column chromatography; b. The products exhibited spectral data in accordance with the proposed structures; c. Transmetalation of the telluroenyne followed by capture with water gave the corresponding tellurium free enyne of E configuration as the main product³; d. Prepared according to reference 10; e. Prepared as described in reference 6; f. Prepared as described in reference 3.

Acknowledgments: The authors thank the following agencies for support: CNPq, FAPESP and PADCT.

References and Notes

1. For reviews see: a. Petragnani, N. and Comasseto, J.V.; *Synthesis*, 1991, 897. b. Comasseto, J.V.; *Phosphorus and Sulfur*, 1992, **67**, 183.
2. Barros, S.M.; Comasseto, J.V. and Berriel, J.; *Tetrahedron Lett.*, 1989, **30**, 7353.
3. Dabdoub, M.J.; Dabdoub, V.B. and Comasseto, J.V.; *Tetrahedron Lett.*, 1992, **31**, 2261.
4. Comasseto, J.V. and Berriel, J.; *Synth. Commun.*, 1990, **20**, 1681, and corrigenda, 1992, 000.
5. Lipshutz, B.H.; *Synlett*, 1990, 119.
6. Barros, S.M.; Dabdoub, M.J.; Dabdoub, V.B. and Comasseto, J.V.; *Organometallics*, 1989, **8**, 1661.
7. Posner, G.H.; *"An Introduction to Synthesis Using Organocopper Reagents"*; Wiley, New York, 1980.
8. **Typical Procedure:** n-Butyllithium (1.35ml; 2.5mmol of a 1.84M solution in hexane) was added to thiophene (0.21g; 2.5mmol) in THF (2ml) in a 10 ml 2-necked flask under nitrogen at -70°C. The temperature was allowed to reach 0°C, while stirring was maintained for 30 min. The yellowish solution was then transferred via cannula into a 25 ml, 2-necked flask containing CuCN [0.18g; 2.0mmol of a commercial (Aldrich) sample, dried over P₂O₅ under vacuum in an Abderhalden apparatus] and THF (3ml), previously purged with nitrogen and cooled to -70°C. Warming to 0°C produces a homogeneous solution which was recooled to -70°C. n-Butyllithium (1.1ml; 2.0mmol of a 1.84M solution in hexane) was added. Stirring was continued for 15 min and then the mixture was allowed to reach room temperature. The bis-vinyl telluride (1.1mmol) in THF (2ml) was added, the solution was stirred for 1 h and then cooled to -70°C and the enone (2.0mmol) was added via syringe. The cooling bath was removed and the solution was stirred for 20 min at room temperature. The reaction was quenched with a 4:1 mixture of saturated aqueous ammonium chloride and ammonium hydroxide, and extracted with ethyl acetate (30 ml). The organic layer was separated, washed with brine (2 X 50ml) and dried over MgSO₄. The solvent was evaporated and the residue was chromatographed in silica-gel eluting first with hexane and then with hexane/ethyl acetate (5:1), giving the desired 1,4 addition product with the yields shown in Tables 1 and 2. The residue from entries 9, 10, 15 and 16 (table 1) were chromatographed eluting first with hexane and then with ethyl acetate.
9. Wakefield, B.J.; *"Organolithium Methods"*; Academic Press, London, 1988.
10. Dabdoub, M.J.; Dabdoub, V.B.; Comasseto, J.V. and Petragnani, N.; *J. Organomet. Chem.*, 1986, **308**, 211.
11. **Typical Procedure:** To a stirred suspension of CuCN [0.089g; 1.0mmol of a commercial (Aldrich) sample dried over P₂O₅ under vacuum in an Abderhalden apparatus] in THF (3ml), under N₂ cooled to -70°C, was added n-butyllithium (1.1ml; 2.0mmol of a 1.84M solution in hexane). The resulting homogeneous solution was stirred for 30 min at -70°C and then allowed to reach room temperature. A solution of vinyl thienyl telluride (1.0mmol) in THF (2ml) was added. After 1 h the reaction mixture was cooled to -70°C, the neat enone (1.0mmol) was added and the mixture was stirred for 20 min at room temperature. The reaction was quenched with a 4:1 mixture of saturated aqueous ammonium chloride and ammonium hydroxide, and extracted with ethyl acetate (15 ml). The organic layer was separated, washed with brine (2 X 25ml) and dried over MgSO₄. The solvent was evaporated and the residue was purified by chromatography on silica-gel, eluting first with hexane and then with hexane/ethyl acetate (5:1) giving the 1,4 addition product with the yields indicated in Table 2.

(Received in USA 19 May 1992; accepted 30 June 1992)