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Communication

Substitution Reaction Between Functionalized *Z*-Vinylic Tellurides and Lower Order Cyanocuprates. Synthesis of *Z* or *E* α,β Unsaturated Esters Using the Same *Z*-Vinylic Telluride

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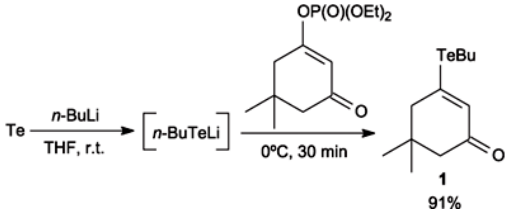
A reação de substituição entre cianocupratos de ordem inferior e teluretos vinílicos funcionalizados *Z* foi estudada. Cetonas cíclicas α,β-insaturadas foram obtidas em excelentes rendimentos. Mudanças nas condições da reação forneceram ésters α,β-insaturados com alta diastereosseletividade.

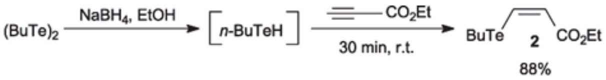
The substitution reaction between lower order cyanocuprates and functionalized *Z*-vinylic tellurides was investigated. α,β-Unsaturated carbonyl compounds were obtained in excellent yields. Changes in the reaction conditions afforded α,β-unsaturated esters in high diastereoselectivity.

Keywords: tellurides, cyanocuprates, α,β-unsaturated esters, α,β-unsaturated ketones, diastereoselective synthesis

The diastereoselective synthesis of α,β-unsaturated ketones and esters constitutes a challenge to organic chemists due to their synthetic applications.[1] Several procedures have been described for the synthesis of these compounds[2] but a general and highly diastereoselective alternative route would still be desirable. In view of our longstanding interest in organic tellurium chemistry,[3] we decided to explore some special features of the compounds of this element to prepare α,β-unsaturated carbonyl compounds. *Z*-Vinylic tellurides have been the most explored organotellurium compounds due to their ability to generate other reactive organometallic compounds, mainly through copper chemistry,[3,4] and to perform several coupling reactions.[5] Cross-coupling reaction between *Z*-vinylic tellurides and cyanocuprates takes place when at least one gegenion in the higher order cyanocuprate is $MgBr^+$.[6] At the same time, the coupling is also observed when both cations (Li^+ or $MgBr^+$) are present in the lower order cyanocuprate, affording disubstituted olefins.[7] An important feature of all these reactions is that the Z stereochemistry of the double bond is maintained. In this way, functionalized *Z*-vinylic tellurides could be interesting precursors of α,β-unsaturated systems with defined stereochemistry. In order to test this idea two functionalized vinylic tellurides (1 and 2) were prepared and reacted with lower order cyanocuprates. Telluride **1** was prepared through vinylic substitution reaction of the corresponding enol phosphate,[9] by lithium butyltellurolate (Scheme 1)[8] and telluride **2** was synthesized by hydrotelluration[10] of ethyl propiolate (Scheme 2).[11]



Scheme 1.



Scheme 2.

Tellurides **1** and **2** were reacted at room temperature with lithium cyanocuprates **3**, generated *in situ* from the slow addition of one equivalent of an alkyllithium to a suspension of CuCN in THF at –78 ºC, affording the corresponding products **4** and **5**, respectively. The products were purified and isolated by column chromatography in good to excellent yields (Scheme 3 – Table 1).[12]

The reaction was fast in all cases, reaching the completion at room temperature in 5 and 10 minutes for tellurides **1** and **2,** respectively. When the reactions were performed with acyclic telluride **2**, leading to **5b** and **5c**, the products formed presented total inversion of the *Z* configuration of the double bond, giving

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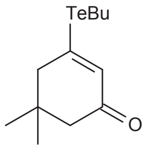
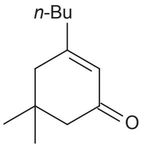
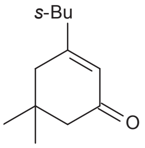
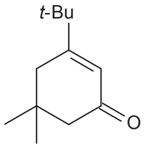
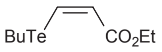
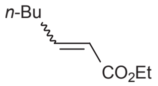
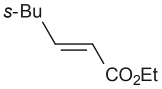
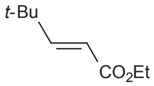
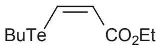
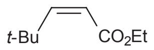
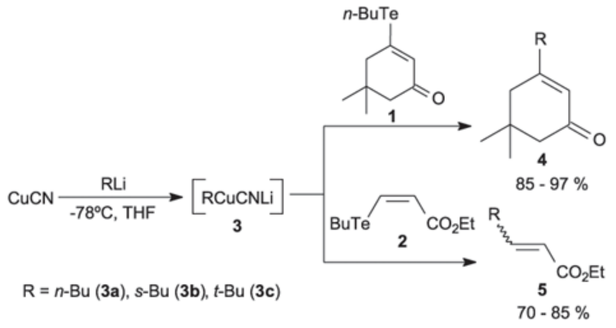
Table 1. Products of the substitutiton reaction between functionalized *Z*-vinylic tellurides and lower order cyanocuprates

Temperature	**Tellurides**	**Products**[a]		
r.t.	 **1**	 **4a** (85%)	 **4b** (83%)	 **4c** (97%)
r.t.	 **2**	 **5a** (73%) 4:1 (*E*:*Z*)	 **5b** (79%) *E*	 **5c** (85%) *E*
–78°C ⇓ 0°C	 **2**	 **5d** (70%) *Z*	 **5e** (72%) *Z*[b]	 **5f** (81%) *Z*[b]

[a] all compounds presented analytical data in accordance with the proposed structures; [b] traces of the *E* isomer were detected by GC-MS.



Scheme 3.

E α,β-unsaturated esters. On the other hand, product **5a** was obtained as a 4:1 mixture of *E* : *Z* olefins.

Changing the telluride addition temperature from room temperature to –78 °C, not surprisingly the reaction time increased. Due to the need for longer reaction times to have total consumption of telluride **2** as well as to the instability of cyanocuprates **3**, the reactions were allowed to warm up to 0 °C after the addition of the telluride.[13] Under these conditions, the total consumption of telluride **2** ocurred in 20 minutes, and the products **5d-f** showed the *Z* configuration (>99% selectivity). By GC-MS analysis, it was possible to detect traces of the *E* isomers in the crude mixtures of compounds **5e** and **5f**.

In conclusion, functionalized *Z*-vinylic tellurides react efficiently with lower order cyanocuprates in good yields. Depending on the reaction temperature, the product geometry present inversion or retention of the double bond configuration of the starting telluride. This stereochemistry control makes this method unique, allowing the synthesis of the *Z* or the *E* α,β-unsaturated carbonyl compounds only by changing the reaction temperature.

Acknowledgements

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12. General procedure for substitution reactions between functionalized tellurides and lower order cyanocuprates at room temperature: To a suspension of dry CuCN (0,089 g; 1 mmol) in THF (10 mL), under nitrogen at -78 ºC was slowly added alkyllithium (1 mmol). The reaction was stirred at this temperature for 20 min and a limpid and clear solution was obtained. The mixture was allowed to reach room temperature and the corresponding telluride (1 mmol) was added. The reaction was monitored by TLC, until the consumption of the telluride. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with a 1:1 solution of saturated aqueous NH_4Cl and NH_4OH (4 x 50 mL). The organic phase was dried with magnesium sulfate and the solvents were evaporated. The residue was purified by silica gel column chromatography eluting with hexane:ethyl acetate (9:1). *(E)-ethyl 4-methylhex-2-enoate* (**5b**). (0.123 g, 79%) [78023-52-6]. IR ν_{max}/cm^{-1}: 2965, 2932, 2877, 1721, 1653, 1461, 1269, 1186, 1136, 1042 (neat). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 (dd, *J* 15.7 Hz, 7.8 Hz, 1H), 5.78 (dd, *J* 15.7 Hz, 1.2 Hz, 1H), 4.18 (quart., *J* 7.1 Hz, 2H), 2.24-2.19 (m, 1H), 1.40-1.34 (m, 2H), 1.29 (t, *J* 7.1 Hz, 3H), 1.04 (d, *J* 6.7 Hz, 3H), 0.88 (t, *J* 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 154.4, 119.8, 60.2, 38.2, 28.9, 19.2, 14.3, 11.6. LRMS *m/z* (rel. int.) 156 (M^+, 20), 128 (14), 111 (41), 95 (34), 82 (40), 69 (40), 55 (100).
13. General procedure for substitution reactions between functionalized tellurides and lower order cyanocuprates at low temperatures: To a suspension of dry CuCN (0,089 g; 1 mmol) in THF (10 mL), under nitrogen at -78 ºC was slowly added alkyllithium (1 mmol). The reaction was stirred at this temperature for 20 min and a limpid and clear solution was obtained. Then the corresponding telluride (1 mmol) was added and the reaction was warmed up to 0 ºC. The reaction was maintained at this temperature and monitored by TLC, until the consumption of the telluride. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with a 1:1 solution of saturated aqueous NH_4Cl and NH_4OH (4 x 50 mL). The organic phase was dried with magnesium sulfate and the solvents were evaporated. The residue was purified by silica gel column chromatography eluting with hexane:ethyl acetate (9:1). *(Z)-ethyl 4-methylhex-2-enoate* (**5e**). (0.112 g, 72%) [169735-64-2]. IR ν_{max}/cm^{-1}: 2966, 2933, 1723, 1645, 1416, 1188, 1131, 1035 (neat). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (dd, *J* 11.5 Hz, 10.2 Hz, 1H), 5.71 (dd, *J* 11.5 Hz, 0.8 Hz, 1H), 4.16 (quart., *J* 7.1 Hz, 2H), 3.45-3.35 (m, 1H), 1.44-1.31 (m, 2H), 1.28 (t, *J* 7.1 Hz, 3H), 1.00 (d, *J* 6.6 Hz, 3H), 0.87 (t, *J* 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 155.9, 118.5, 59.7, 34.4, 29.8, 19.9, 14.2, 11.7. LRMS *m/z* (rel. int.) 156 (M^+, 28), 128 (22), 111 (44), 95 (33), 82 (40), 69 (37), 55 (100).

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