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INFLUENCE OF THE GEGENION IN THE TRANSMETALATION REACTION OF VINYLIC TELLURIDES WITH HIGHER ORDER CYANOCUPRATES[1]

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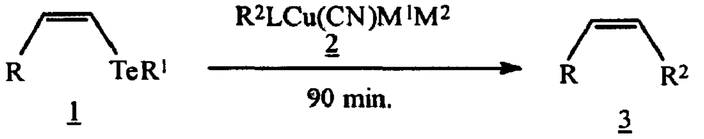
Key Words : Vinylic tellurides, transmetalation, cross-coupling.

Abstract: Dilithium cyanocuprates $R^2LCu(CN)Li_2$ (L=2-Th, Me) react with vinylic tellurides of **Z** configuration, $RCH{=}CHTeR^1$ to give higher order vinylic cyanocuprates, $[(RCH{=}CH)LCu(CN)Li_2]$. By changing the gegenion from lithium to magnesium $[R^2LCu(CN)LiMgBr$ or $R^2LCu(CN)(MgBr)_2]$ the reaction gives cross - coupling products of **Z** configuration, $RCH{=}CHR_2$ in good yields.

Transmetalation reaction of organometallic precursors with easily prepared organocuprates[2] emerged in recent years as a source of organocopper reagents of more complex structure.[3] Of particular importance are the transmetalations of vinylic derivatives of boron,[4] tin,[6] aluminum[7] and zirconium,[8] which found use in the synthesis of complex natural products.[3] In our laboratory it was observed that vinylic tellurides of **Z** configuration efficiently transmetalate with $Me_2Cu(CN)Li_2$ and $Bu(2\text{-}Th)Cu(CN)Li_2$ to give the **Z**-vinylic cyanocuprates, which react with enones[9] and epoxides[10] leading respectively to 4,5-unsaturated ketones or homoallylic alcohols in good yields. This reaction is unique in the sense that the generated vinylic cuprates exhibit the **Z** configuration, as a consequence of the *trans* addition nature of the hydrotelluration of acetylenes, which leads to the exclusive formation of the **Z** vinylic tellurides,[11] in contrast with the hydroboration,[4] hydrostanation,[5] hydroalumination[7] and hydrozirconation[8] of acetylenes, which give the **E** olefin.

In the course of our initial studies on the transmetalation reaction of vinylic tellurides 1 with cyanocuprates 2 we observed the formation of the olefin 3 as by-product in some reactions with enones.[9] By refluxing the reaction mixture in the absence of the enone, the olefin 3 was the main product formed in reasonable yields and with retention of the **Z** configuration (Eq.1; $M^1 = M^2 = Li^+$; $R^2 = n\text{-}C_4H_9$; L = 2-Th, $n\text{-}C_4H_9$, reflux).



(1)

By changing the gegenion (M^1,M^2) from Li^+ to $MgBr^+$ the olefin 3 was the only product obtained in high yields at room temperature, even when an enone was added to the reaction mixture. The influence of the gegenion, the Grignard reagent, the ligand and the structure of the vinylic telluride in this novel cross-coupling reaction is shown in Tables 1, 2 and 3.

Table 1 - Influence of the gegenion in the reaction of vinylic tellurides with higher order cyano cuprates. (Eq. 1: R = C_6H_5, R^2 = n-C_4H_9, r.t.)

R^1	L	M^1	M^2	Yield(%)
1. $C_6H_5CH=CH$	n-C_4H_9	Li	Li	trace^b
2. $C_6H_5CH=CH$	2-Th	Li	MgBr	90^a
3. $C_6H_5CH=CH$	n-C_4H_9	Li	MgBr	95^a
4. $C_6H_5CH=CH$	n-C_4H_9	MgBr	MgBr	95^a
5. C_6H_5	n-C_4H_9	Li	Li	trace^b
6. C_6H_5	2-Th	Li	MgBr	63^a
7. C_6H_5	n-C_4H_9	Li	MgBr	75^a
8. C_6H_5	n-C_4H_9	MgBr	MgBr	90^a
9. n-C_4H_9	n-C_4H_9	Li	Li	trace^b
10. n-C_4H_9	2-Th	Li	MgBr	60^a
11. n-C_4H_9	n-C_4H_9	Li	MgBr	74^a
12. n-C_4H_9	n-C_4H_9	MgBr	MgBr	88^a

a) isolated yields; b) by GC-MS.

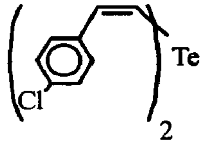
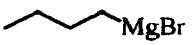
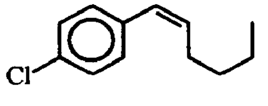
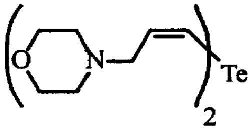
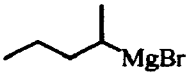
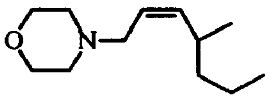
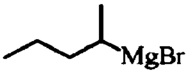
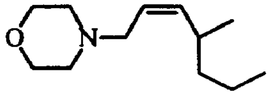
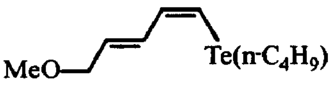
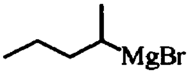
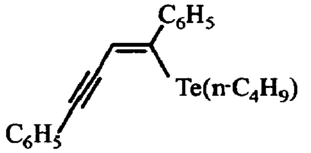
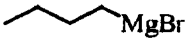
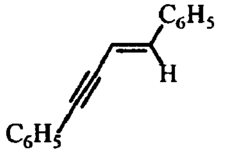
No difference in yields was observed in changing the ligand from 2-Th for n-C_4H_9. The yields dropped when R^1 was changed, the vinylic tellurides containing a phenyl or a butyl group linked to tellurium affording lower yields than the one containing the styril group. In all cases where M was $MgBr^+$ the yields were high, decreasing when one of the gegenions was Li^+. When both were Li^+ only trace of the olefin 3 was obtained.

Table 2 - Influence of the Grignard reagent (Eq. 1: L = R^2, M^1 = M^2 = $MgBr^+$, r.t.)

R^1	R^2	Yield (%)
1. $C_6H_5CH=CH$	n-C_4H_9	95^a
2. $C_6H_5CH=CH$	s-C_5H_{11}	82^a
3. $C_6H_5CH=CH$	C_6H_5	78^b
4. $C_6H_5CH=CH$	$CH_3CH=CH$	23^b
5. C_6H_5	n-C_4H_9	90^a
6. C_6H_5	s-C_5H_{11}	80^a
7. C_6H_5	$CH_3CH=CH$	$40(68^c)^b$
8. C_6H_5	C_6H_5	84^b
9. n-C_4H_9	n-C_4H_9	88^a
10. n-C_4H_9	s-C_5H_{11}	75^a
11. n-C_4H_9	C_6H_5	70^b
12. nC_4H_9	$CH_3CH=CH$	25^b

a) isolated yields; b) GC yields c) 100% excess of the cuprate 2 n-Butyl, s-pentyl and phenyl Grignard reagents gave good yields of the olefin 3, whereas vinyl Grignard reagents only gave reasonable yields when a 100% excess of the reagent was used (entry 7, Table 2).

Table 3 - Influence of the structure of the vinylic tellurides in the reaction course (Eq. 1: L = R^2, $M^1 = M^2 = MgBr^+$, r.t.).[12]

	Telluride[13]	Grignard Reagent	Product	Yield (%)
1.				90^a
2.				$15^{b,c}$
3.				75^a
4.				70^a
5.		C_6H_5MgBr		68^b
6.				80^a

a) isolated yields; b) GC yields; c) the starting material was recovered

The bis-vinylic telluride[14] (entry 2, Table 3) gave low yield of the cross-coupling product, whereas the analogous butyl-vinyl telluride (entry 3, Table 3) gave this product in high yield. The telluroenyne (entry 6, Table 3) underwent a transmetalation reaction instead of a cross-coupling, presumably due to steric reasons. An important aspect to be pointed out is that the tellurium-phenyl bond was not affected when $MgBr^+$ was one of the gegenions (entries 5-8, Table 2) in contrast with the reaction using Li^+ as gegenions, when the tellurium-vinyl and tellurium-phenyl bonds were both transmetalated.[9]

The results discussed above show that the vinylic tellurides react with higher order cyanocuprates in different ways, depending on the gegenion present in the cuprate. Probably the vinylic telluride 1 forms an "ate" complex with the higher order cyanocuprate 2, which undergo a transmetalation leading to a vinyl cyanocuprate when both cations are Li^+ or to the cross coupling product 3 (eq. 1) when one or both cations are MgX^+.

Besides the systematic aspects of the reaction reported in this communication, its synthetic importance must be considered, since it consists in the cross-coupling of a Grignard reagent with a vinylic telluride mediated by a lower order cyano cuprate, affording a route to disubstituted olefins of **Z** configuration.

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Reference and Notes

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12. **Typical Experiment:**To a stirred suspension of CuCN [2.6 mmol; 0.232 g of a commercial (Aldrich) sample dried over P_2O_5 under vacuum in an Abderhalden apparatus] in THF (8 ml), under N_2 at 0°C was added butylmagnesium bromide (5.6 mmol; 5.6 ml of a 1.0 M solution in THF). Stirring was continued until a homogeneous solution has been produced (~15 min.). The cooling bath was removed and the solution warmed to room temperature. A solution of butyl-styryl telluride (2.0 mmol; 0.576 g) in THF (5 ml) was then added and the resulting solution stirred for additional 90 min. at this temperature. Quenching was carried out using saturated aqueous NH_4Cl solution (50 ml) followed by extraction with ether (2 x 25 ml). The extracts were washed with brine, the solid residues[15] were removed by filtration and the clean solution dried over $MgSO_4$. The solvent was removed and the residue was partially purified by chromatography on silica-gel eluting with hexane. The yield was determined by G.C. of this chromatographed sample. *Cis* 1-phenyl-1-hexene was obtained chromatographically pure after horizontal distillation of the chromatographed sample under reduced pressure.
13. Prepared according to literature procedures[11].
14. X-ray analysis of this compound showed a "nest"conformation, containing five atoms with lone electron pairs (Schpector, J. Z., Chieffi, A., Tucci, F. C. and Comasseto, J.V., to be published)
15. By treating this solid residue with ammonium chloride the corresponding diorganoditelluride (R^1TeTeR^1) was formed.

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