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Palladium-catalyzed cross-coupling reactions of dimethyl- and diethylzinc with unsaturated organotellurium compounds†

Miguel J. Dabdoub,[a,*] Vânia B. Dabdoub[b] and Joseph P. Marino[b,*,‡]

[a]*Laboratório de Síntese de Compostos Organocalcogênios, Departamento de Química, FFCLRP, Universidade de São Paulo,*
Av. Bandeirantes, 3900 Ribeirão, Preto-SP, Brazil
[b]*Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109, USA*

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Abstract

The cross-coupling reaction of diethyl- or dimethylzinc compounds with disubstituted vinylic tellurides as electrophilic partners is described. These cross-coupling reactions were catalyzed by $Pd(PPh_3)_4$/CuI and were shown to be general, allowing the formation of a new sp^3–sp^2 carbon–carbon bond. Good yields and high stereoselectivity were observed in all cases. © 2000 Elsevier Science Ltd. All rights reserved.

It has long been recognized that organotellurium species are an efficient source of aryl,[1a] benzyl,[1a,b] allyl,[1a,b] alkyl,[1a] alkynyl[1a,c,d] and vinyllithium[1a,b,2] or vinylcopper[2b,3] intermediates by means of the Te/metal-exchange. Other Te/metal-exchange reactions are currently attracting the interest of chemists due to the special regio- and stereoselectivity properties which are unique to tellurium species. Recently, Kambe et al.[4] have described the transmetalation of trisubstituted vinylic tellurides to the corresponding ethylvinylzinc reagents by reaction with diethylzinc in THF at room temperature. Engman et al.[5] observed that the transmetalation of diaryl tellurides and diaryl ditellurides with Et_2Zn only occurred in the presence of catalytic amounts of $Ni(acac)_2$ leading to mixed ethyl arylzinc derivatives. Even more recently (1998), Uchiyama et al.[6] studied the Te/Zn-exchange reaction in the 2-butyltelluropyridine. They observed that while this alkyl aryl telluride did not react with lithium trimethyl zincate (rt, 18 h), the reaction with dilithium tetramethyl zincate (Me_4ZnLi_2) proceeded smoothly at 0°C (2 h) affording the mixed dilithium 2-pirydinyltrimethyl zincate intermediate.

As part of our efforts toward the total synthesis of polyene-containing natural products, we required an efficient cross-coupling methodology for the stereoselective synthesis of diene and polyene systems. Due to the easy availability of methods to obtain vinylic tellurides of defined configuration,[2a] we directed our efforts at expanding the scope of the Te/Zn transmetalation as described by Kambe et al.,[4] pursuing

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[*] Corresponding authors. E-mail: migjodab@usp.br (M. J. Dabdoub)

[†] In memory of Professor José Tércio B. Ferreira.

[‡] E-mail: jpmarino@umich.edu

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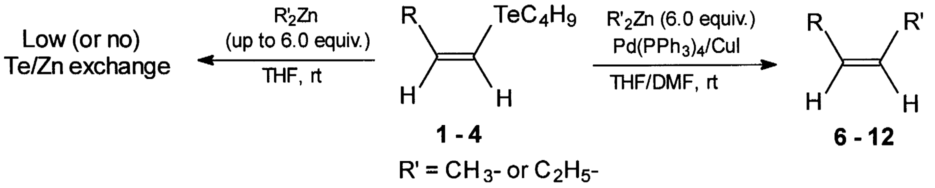
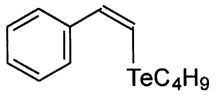
the use of the generated vinylzinc reagents in the palladium-catalyzed cross-coupling reaction with vinyl halides in a modified Negishi's cross-coupling process.[7] However, all the attempts to carry out the Te/Zn-exchange reaction of disubstituted vinylic tellurides with diethylzinc in THF at room temperature failed to work in our chosen vinylic tellurides. We now describe our results concerning this reaction and the palladium-catalyzed cross-coupling reaction of dialkylzinc reagents with vinylic tellurides. Our studies provide a modification of the experimental conditions in an attempt to perform the Te/Zn-exchange reaction in an efficient manner (Scheme 1).

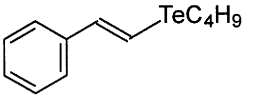


Scheme 1.

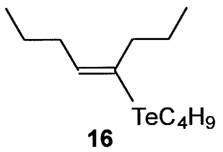
Despite extensive investigation of various substrates (compounds **1**–**5**, **14**–**16**), different amounts of Et_2Zn or Me_2Zn[8] (up to 6.0 equiv.) and reaction times (up to 24 h), no synthetically useful yields (<20%) were obtained using the described approach.[4] It was considered that the steric bulkiness of the R group in a *cis* orientation to the butyltellurium group could be responsible for the slow Te/Zn-exchange reaction.[4] Consequently, the reactions of compounds **14** and **15** were carried out under literature conditions[4] to compare the reactivity when the butyltellurium group is in a *trans*- or in a *cis*-relation to the group attached to the adjacent carbon. However, these reactions with 1.0, 2.0, 5.0 and 6.0 equiv. of Et_2Zn (5 h up to 24 h) did not occur even with the *trans*-isomer **15**. In these cases, the starting materials were almost completely recovered.



14



15



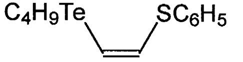
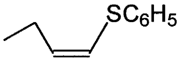
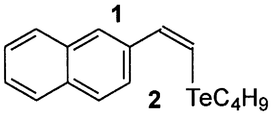
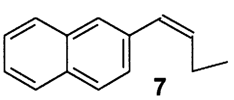
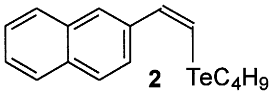
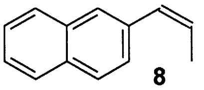
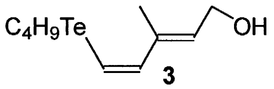
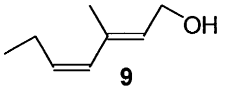
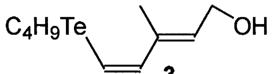
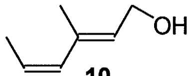
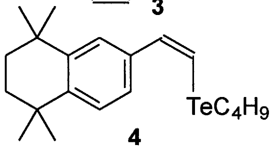
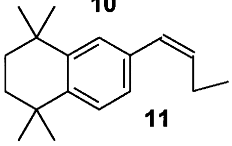
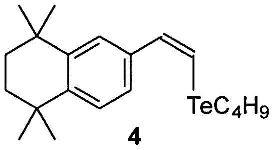
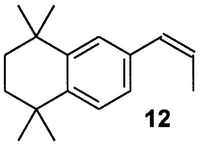
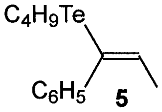
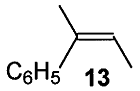
16

Trisubstituted vinylic tellurides **5** and **16** were also allowed to react with Et_2Zn in THF. Compound **16** was detellurated in 10% yield (Et_2Zn in toluene, 2.0 equiv., 5 h) and in 15% yield (E_2tZn in toluene, 6.0 equiv., 5 h) only. In the case of compound **5**, which contained a phenyl group attached to the carbon bearing the butyltellurium moiety, the reaction occurred to a considerably larger extent (55%) as confirmed by ^1H NMR analysis of the crude mixture (2.0 equiv. of Et_2Zn in hexane, 5 h rt)[9] although it was not complete even when 6.0 equiv. of Et_2Zn in toluene was used (rt, 5 h). We assume that these facts indicate that the Te/Zn-exchange reaction occurred with the examples described by Kambe et al.[4] because all the vinylic tellurides employed by these authors had a group (phenyl, ester or trimethylsilyl) that could stabilize the vinylzinc formed in the α-position.

During our experimental work, we decided to investigate different experimental conditions. The addition of $Pd(PPh_3)_4$ and the use of DMF as co-solvent resulted in the formation of the corresponding methylated or ethylated products. However, the transformation of the starting material was still incomplete. The addition of CuI (1.0 equiv.) proved to be beneficial in bringing the cross-coupling reaction to completion (4 h, rt). In our reaction no use of LiCl was necessary, as is the case for the Stille[10] reaction. Our cross-coupling reaction required the use of an excess of dialkylzinc reagent (4–6 equiv.) and was carried out[11] with a series of vinylic tellurides (Table 1, Scheme 1).

To confirm the necessity of the $Pd(PPh_3)_4$ as a catalyst and the accelerating effect we decided to carry

Table 1
Cross-coupling products obtained using dialkylzinc compounds and vinylic tellurides

Entry	Zinc reagent	Electrophile	Product	Yield (%)[a]
1	$C_2H_5)_2Zn$	 **1**	 **6**	69
2	$C_2H_5)_2Zn$	 **2**	 **7**	73
3	$CH_3)_2Zn$	 **2**	 **8**	92
4	$C_2H_5)_2Zn$	 **3**	 **9**	71
5	$CH_3)_2Zn$	 **3**	 **10**	82
6	$C_2H_5)_2Zn$	 **4**	 **11**	78
7	$CH_3)_2Zn$	 **4**	 **12**	83
8	$CH_3)_2Zn$	 **5**	 **13**	$33^{b,c}$ $42^{b,d}$

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[a] In reactions with diethylzinc a small amount of the starting material (ca. 5-10%) always remain unreacted while in reaction with dimethylzinc the complete transformation was observed following the reactions by TLC. [b]Transformation determined by ^1H NMR (no total transformation of the starting material was observed). [c]Using 6.0 equiv of Me_2Zn (4h, rt) [d]Using 10 equiv. of Me_2Zn (10h, rt).

out the reaction in the absence of this compound, but still in the presence of CuI. In this case, removal of the butyltellurium group becomes the preferred reaction. The role of CuI was critical and hypothetically the reaction pathway was based on the formation of a copper intermediate by transmetalation of the dialkylzinc reagent.

In summary, we have shown that the Te/Zn-exchange reaction using Et_2Zn is not a general method to obtain vinylzinc reagents; however, a new carbon–carbon bond is formed when the reaction is carried out employing the $CuI/Pd(PPh_3)_4/DMF$ system. It is evident from the results presented here, and in the accompanying communication, that our palladium-catalyzed cross-coupling could be potentially useful for other kinds of carbon–carbon bond formation. In this context, we are currently investigating a different Te/Zn transmetalation protocol to obtain vinylzinc intermediates and the cross-coupling reactions involving the latter species will be reported in due course.

Acknowledgements

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8. Different presentations of Et_2Zn used in this work were purchased from Aldrich as solutions in hexane (1.0 M), in toluene (1.1 M) or neat. Similar results were obtained using Me_2Zn (2.0 M in toluene).
9. Different results were obtained using neat Et_2Zn or a solution (1.0 M) of this reagent in toluene.
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11. Typical procedure: To a solution of compound **2** (1.0 mmol) in THF (5 mL), $Pd(PPh_3)_4$ (0.055 g; 0.05 mmol), CuI (0.19 g, 1.0 mmol) and DMF (5 mL) were added at room temperature under N_2. Then a commercial dimethylzinc solution (3.0 mL) (2.0 M, in toluene) was transferred dropwise via syringe. The dark brown resulting mixture was stirred for 3 h (followed by TLC) and was carefully treated with water and extracted with diethyl ether. The product was purified by column chromatography using hexane as eluent.