Hydrozirconation of Stannylacetylenes. Synthesis and Reactions of Ketene Stannyl(Telluro) Acetals†

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Stannylacetylenes **7a**−**e** react with $Cp_2Zr(H)Cl$ in THF at room temperature to give the α-zirconated vinylstannane intermediates **8a**−**e**, which subsequently react with butyltellurenyl bromide (2.0 equiv) to give exclusively ketene stannyl(telluro) acetals **6a**−**e** of *E* configuration. Similar reactions were performed using phenylselenenyl bromide (2.0 equiv) as the electrophile, but a mixture of products was formed including the expected ketene stannyl(seleno) acetals **12**. Otherwise, the use of 1.4 equiv of $Cp_2Zr(H)Cl$ and 1.0 equiv of PhSeBr results in the exclusive formation of **12**, in good yields. Treatment of ketene stannyl(telluro) acetals with iodine or NBS followed by reductive dehalogenation results in the formation of 1-iodo-1-telluroalkenes **4a**−**e** and 1-bromo-1-telluroalkenes **5a**−**e**, respectively, with total retention of the configuration.

Introduction

Methodologies for the synthesis of enyne compounds are of great interest, especially with regard to synthesis of enediyne[1] and dienediyne[2] antibiotics or related molecular models.[3] These antibiotics have been isolated from a variety of natural sources and possess strong antibacterial, antifungal, anticancer, and antiviral activities including the ability to cleave DNA.[4−6] Calicheamicins, esperamicin, dynemicin A, Kedarcidin chromophore, and C-1027 chromophore are examples of enediyne antibiotics[1,4,5] while Neocarzinostatin chromophore[7] and Thiaru-

bines[2,6] are examples of dienediyne antibiotics. A wide range of natural *trans*-enynes and *cis*-enynes were isolated from Laurencia red algae[8] or from a green variety of the Hawaiian algae *Laurencia nidifica*.[9] *cis*-Enynes were also obtained from seahares,[10] sponges,[11] or South American "poison arrow" frogs.[12]

Vinylstannanes have numerous uses in organic synthesis.[13] These compounds can be prepared by direct hydrostannation of alkynes; however, this route is generally not stereoselective.[14] The tin/lithium transmetalation reaction with alkyllithium is one of the most direct approaches to vinyllithium reagents.[13,15] The palladium-catalyzed coupling reaction of organostannanes with organic halides or sulfonates known as Stille coupling has already been established as an efficient stereospecific method for the formation of carbon−carbon bonds under mild conditions.[16] On the other hand, there has been

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remarkable interest in the synthesis of vinylic tellurium species and their synthetic applications because the tellurium moiety can be replaced by different organic groups always with total retention of the configuration. Most of these reactions involve transmetalation to form the corresponding lithium,[17] copper,[18] magnesium,[19] calcium,[19] sodium,[19] or zinc[20] vinylic intermediates. However, limited reports on the synthesis of highly functionalized vinylic tellurides have appeared in the literature.[21]

As demonstrated in previous papers, we have special interest in the synthesis[17e,g] and reactions[17e,g,j,22] of tellurobutenyne systems with a defined configuration at the generated double bond, because these compounds permit the synthesis of enynes[17e,j] and enediynes[18e,23] via lithium, copper, or zinc intermediates with total retention of the configuration. To date, a method to obtain the 1-(organyltelluro)-1-buten-3-ynes **1** has been described,[17e,g,j] but 2-(organyltelluro)-1-buten-3-ynes **2** or **3** are unknown.
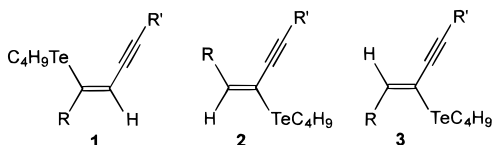
In connection with other research currently underway in our laboratory (for the preparation and uses of compounds **2**), we required a method for the preparation of the unknown bifunctionalized vinylic tellurides of types **4**–**6**. Different reactivities between halogen (or the tin moiety) and the tellurium group in the reactions of **4**–**6** could be anticipated. Therefore, the synthesis of isomerically pure α-halovinyl tellurides **4** and **5** is of great interest to us and for future uses in organic synthesis. These compounds could be transformed to the corresponding telluroenynes **2** via cross-coupling reactions catalyzed by transition metals.

Results and Discussion

We report here optimal experimental conditions for the 100% stereoselective synthesis of 1-iodo-1-(butyltelluro)-

Table 1. (E)-Ketene Stannyl(telluro) Acetals Obtained from Stannylacetylenes

Entry	Alkynes	Reaction time (min)	Product[a]	Yield (%)[a]
1	HC≡CSn(C$_4$H$_9$)$_3$ **7a**	15	**6a**	60
2	C$_4$H$_9$C≡CSn(C$_4$H$_9$)$_3$ **7b**	15	**6b**	81
3	C$_6$H$_{13}$C≡CSn(C$_4$H$_9$)$_3$ **7c**	15	**6c**	78
4	C$_6$H$_5$C≡CSn(C$_4$H$_9$)$_3$ **7d**	20	**6d**	70
5	C≡CSn(C$_4$H$_9$)$_3$ **7e**	30	**6e**	74

[a] Isolated, pure materials.

ethenes **4a**–**e** and 1-(bromo-1-butyltelluro)ethenes **5a**–**e** by the halogenolysis of the novel 1-(tributylstannyl)-1-(butyltelluro)ethenes **6a**–**e** which were stereoespecifically obtained by hydrozirconation/telluration of stannylacetylenes.
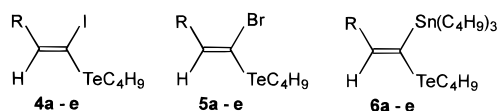
Lipshutz et al. described the hydrozirconation of (trialkylstannyl)acetylenes (R′C≡CSnR$_3$) with Cp$_2$Zr(H)Cl followed by aqueous workup to synthesize vinylstannanes of Z configuration.[24] The regiochemistry of this reaction was determined by capturing the α-zirconated intermediate with I$_2$. Hydrozirconation of (tributylstannyl)ethyne (HC≡CSnBu$_3$) was also studied by these authors, and protonolysis of the dimetallo intermediate resulted in the formation of the corresponding vinylstannane.[24] It should be pointed out that the 1,1-dimetallo or 1,2-dimetallo nature of this specific intermediate was not established by these authors.[24,25]

Currently, we performed the hydrozirconation of the (tributylstannyl)acetylenes **7a**–**e** with Cp$_2$Zr(H)Cl in THF at room temperature. The reaction was monitored by TLC using hexane as the eluent, and the complete disappearance of the starting stannylacetylene was observed in all cases using 1.4 equiv of Schwartz's reagent and after the time indicated in Table 1.[26,27] The α-zirconated vinylstannanes **8a**–**e** were allowed to react in situ with butyltellurenyl bromide (2.0 equiv) at 0 °C, followed by NaBH$_4$ treatment to afford the (E)-1-(butyltelluro)-1-(tributylstannyl)-2-organylethenes **6a**–**e** in good yields (eq 1 and Table 1). Lower yields of ketene stannyl(telluro) acetals and also some vinylstannanes were isolated if 1.0 equiv of the butyltellurenyl bromide was employed.

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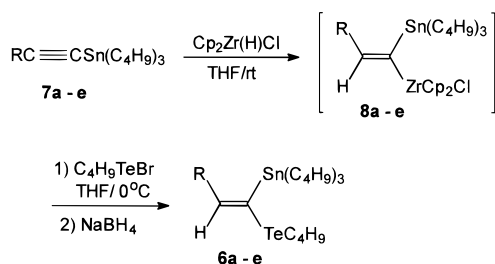
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$$\text{RC}\equiv\text{CSn(C}_4\text{H}_9)_3 \xrightarrow[\text{THF/rt}]{\text{Cp}_2\text{Zr(H)Cl}} \left[\begin{array}{c} \text{R} \quad \text{Sn(C}_4\text{H}_9)_3 \\ \text{H} \quad \text{ZrCp}_2\text{Cl} \end{array}\right]$$

7a - e   **8a - e**

$$\xrightarrow[\text{2) NaBH}_4]{\substack{\text{1) C}_4\text{H}_9\text{TeBr} \\ \text{THF/ 0}^\circ\text{C}}} \begin{array}{c} \text{R} \quad \text{Sn(C}_4\text{H}_9)_3 \\ \text{H} \quad \text{TeC}_4\text{H}_9 \end{array}$$

6a - e

The hydrozirconation of **7a−e** is 100% regio- and stereoselective as previously described.[24,25] We observed that the Zr/Te exchange reaction on intermediates **8a−e** occurs with total retention of the configuration. The stereochemistry for the obtained compounds **6b−e** was confirmed by the NOESY in the ^{1}H NMR spectra. An enhancement of the methylenic protons next to tellurium was observed as the vinylic proton of **6b** was irradiated. There was no correlation between the vinylic proton and CH$_2$ bonded to the tin atom (see the Experimental Section). The correlation between the allylic hydrogens and CH$_2$ of the tributyltin group was also observed. The NOE results indicate that **6b** has the expected *E* configuration. No formation of other isomeric products was detected by the analytical methods employed (^{1}H NMR, ^{13}C NMR, and GC/MS).

The exclusive formation of compound **6a** (entry 1, Table 1) shows that only the 1,1-dimetallo intermediate is formed by the hydrozirconation of (tributylstannyl)ethyne **7a**. The same regiochemistry was observed in the hydrozirconation of (butyltelluro)ethyne, with the zirconium moiety being attached at the α position of the heteroatom.[28] Interestingly, the hydrozirconation of other heterosubstituted terminal acetylenes, such as (trimethylsilyl)ethyne,[29,30] ethoxyethyne,[31,32] and (organylseleno)-ethynes,[28] results in the exclusive formation of the 1,2-dimetallo intermediates because the zirconium moiety is at the β position.

The result described here is in accordance with the significant differences in reactivity between vinylstannanes and vinylzirconates described in the literature.[24,33,34] It was observed that the Zr−Csp^2 bond is more reactive than the Sn−Csp^2 bond, toward cuprate transmetalations[33,34] and iodinolysis.[24]

Unsaturated telluro compounds undergo dihalogenation at the tellurium atom in the presence of a variety of halogenating agents.[22,35−38] However, by treatment with sodium borohydride[17j] or with sodium thiosulfate[17j] the dihalogenated tellurium(IV) compounds are reduced to

Table 2. 1-Telluro-1-haloethenes Obtained from Ketene Stannyl(Telluro) Acetals

entry	reagent	Electrophile	Reaction conditions	Products	Yield (%)[a]
1	6a	I$_2$	0 °C (5 min.) →rt (12 h)	**4a**	56
2	6b	I$_2$	0 °C (3h) → rt (3h)	**4b**	92
3	6c	I$_2$	0 °C (3h) → rt (3h)	**4c**	85
4	6d	I$_2$	0 °C (3h) → rt (3h)	**4d**	81
5	6e	I$_2$	0 °C (3h) → rt (3h)	**4e**	77
6	6a	NBS	0 °C (5 min.) → rt (12h)	**5a**	45
7	6b	NBS	-78 °C (6h)	**5b**	60
8	6c	NBS	-78 °C (6h)	**5c**	55
9	6d	NBS	-78 °C (6h)	**5d**	36
10	6e	NBS	-78 °C (6h)	**5e**	47[b]

[a] Isolated yields. [b] Unstable compound.

the corresponding diorganyl tellurides. Because an excess of BuTeBr (2.0 equiv) is used in our experimental procedure, the crude mixture obtained after workup contains dibutyl ditelluride and the compounds **6a−e** as the dibromotelluro compounds. Thus, treatment of the mixture with NaBH$_4$/EtOH is necessary to isolate the dehalogenated compounds **6a−e** and also to transform the dibutyl ditelluride into the butyltellurolate anion which was captured with butyl bromide to afford dibutyl telluride that is more easily removed by distillation.[28,39]

It is known that some tellurium compounds can undergo tellurium/iodine exchange when reacting with iodine.[38] Similarly, vinylstannanes[13b] can undergo halodestannylation by reactions with iodine,[13b,40,41] bromine,[13b,41] or NBS[13b,41] to afford vinyl halides. In the case of compounds **6a−e**, it was possible to distinguish the differences in reactivity between vinylstannanes and vinylic tellurides because the reaction with excess iodine (2.15 equiv) results in exclusive iodonolysis of the Sn−Csp^2 bond, with the butyltellurium group remaining intact at the double bond (Scheme 1).

After detailed experimental studies, we conclude that the optimal reaction condition is the treatment of compounds **6a−e** with iodine (2.15 equiv) in THF at 0 °C to room temperature under nitrogen by the time indicated in Table 2. Under these conditions was observed the 100% chemoselective reaction that occurs also with total retention of the configuration affording the 1-iodo-1-(butyltelluro)alkenes **4a−e** in good yields (Scheme 1 and

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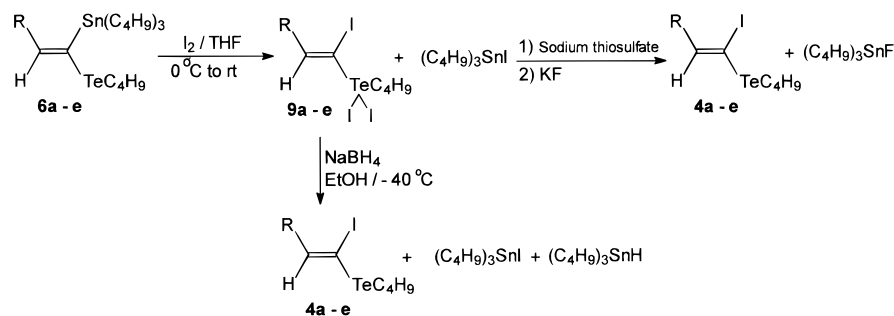(37) Mack, W. *Angew. Chem., Int. Engl. Ed.* **1966**, *5*, 896.

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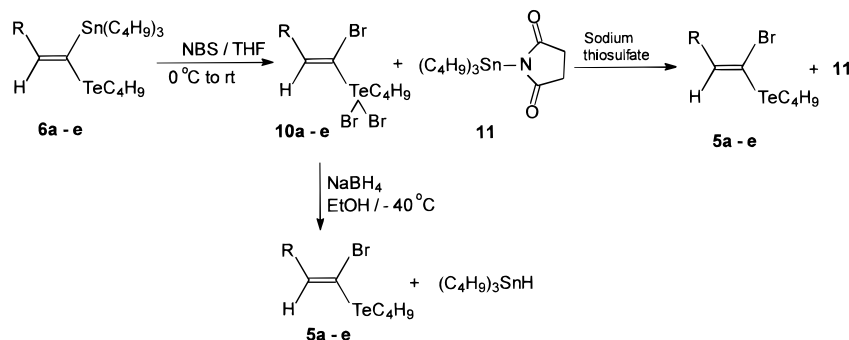
Scheme 1

Scheme 2

Table 2). The stereochemistries of the obtained compounds were confirmed by the measurement of the NOE effects in ^{1}H NMR for **4b** (see the Experimental Section). Other tested reaction conditions gave inferior results. For example, reaction of **6b** and **6c** with 3.0 equiv of iodine in THF under reflux results in formation of the *E*:*Z* stereoisomers (95:5 up to 90:10) as indicated by a new triplet at 7.03 ppm corresponding to the minor undesired isomer in the ^{1}H NMR spectra. When the reaction is performed in THF at 0 °C with 1.5 equiv of iodine, the starting material is partially recovered. Using dichloromethane at 0 °C (instead THF), the reaction with 3.0 equiv of I$_2$ occurs and a partial inversion (ca. 5–10%) on the geometry of the double bond was also observed. When the same solvent (CH$_2$Cl$_2$) is employed at −25 °C this reaction proceeds in good yields with total retention of the configuration even using 3.0 equiv of iodine. However, the long reaction time necessary (overnight) for the total transformation of the starting material is a disadvantage in this case.

Probably, the isomerization of products **9a**−**e** (and consequently **4a**−**e**) in the presence of excess iodine occurs through an addition/elimination process. One significant known feature of iodination of alkenes is that it is easily reversible.[42,43] It had been proven that vicinal diiodides obtained by addition of iodine to olefins can be stored in the dark at −78 °C for days without decomposition; however, at room temperature the diiodides decompose rapidly to the original reactants, and it is accelerated by illumination.[43] Thermal decomposition is also observed in the presence of excess iodine.[44] As observed experimentally by us, the temperature of the reaction and the polarity of the solvent employed play an important role in both reactions: the iododestannylation and the isomerization. The more polar the solvent[45] (CH$_2$Cl$_2$ vs THF) and the higher temperature of the reaction, the faster the isomerization proceeded. However, the observed product ratio did not alter upon extended treatment with excess iodine. The addition/elimination of iodine could

involve charge separation in the transition state,[42a,d] but the hypothesis of a radical mechanism had been considered[43] and could not be disregarded. In an attempt to obtain evidences for the isomerization pathway, the stereochemically pure isomers **6b** and **6c** were reacted with iodine (1.0 up to 3.0 equiv) in THF and CH$_2$Cl$_2$ under different reaction conditions (room temperature and reflux), but no isomerization was observed. From these facts, we suppose that excess iodine together with the presence of the tin species such as BuSnI generated under our reaction conditions could be responsible for the observed isomerization,[46] perhaps through a radical pathway. However, further experiments are necessary to confirm this hypothesis.

The brominolysis of the Sn−Csp^2 bond was achieved in CH$_2$Cl$_2$, employing *N*-bromosuccinimide (3.0 equiv) in most cases at −78 °C (Scheme 2 and entries 7−10 of Table 2). This process occurs also with total retention of the configuration because only formation of compounds **5a**−**e** was observed. NBS was the reagent of choice even with the moderate yields of the obtained products, because the use of Br$_2$ results in a mixture of products.

(42) (a) Robertson, P. W.; Butchers, J. B.; Durham, R. A.; Healy, W. B.; Heyes, J. K.; Johannesson, J. K.; Tait, D. A. *J. Chem. Soc.* **1950**, 2191. (b) Cava, M. P.; Napier, D. R. *J. Am. Chem. Soc.* **1957**, *79*, 1701. (c) Jensen, F. R.; Coleman, W. E. *J. Org. Chem.* **1958**, *23*, 869. (d) Zanger, M.; Rabinowitz, J. L. *J. Org. Chem.* **1975**, *40*, 248.

(43) Skell, P. S.; Pavlis, R. R. *J. Am. Chem. Soc.* **1964**, *86*, 2956.

(44) Ayres, R. L.; Michejda, C. J.; Rack, E. P. *J. Am. Chem. Soc.* **1971**, *93*, 1389.

(45) (a) Empirical measurements of polarity [Eτ(30)] data (for CH$_2$-Cl$_2$, Eτ(30) = 41.1, and for THF, Eτ(30) = 37.4) were abstracted from: Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 98. (b) Dielectric constant (ϵ) data (for CH$_2$Cl$_2$, ϵ = 8.9, and for THF, ϵ = 7.6) were abstracted from: Riddick, J. A.; Bunger, W. B. *Organic Solvents*, 3rd ed.; Techniques of Organic Chemistry; Wiley-Interscience: New York, 1970; Vol. II.
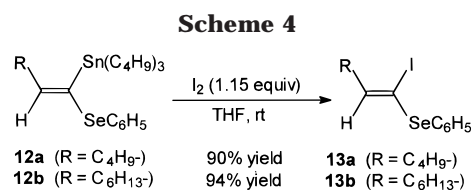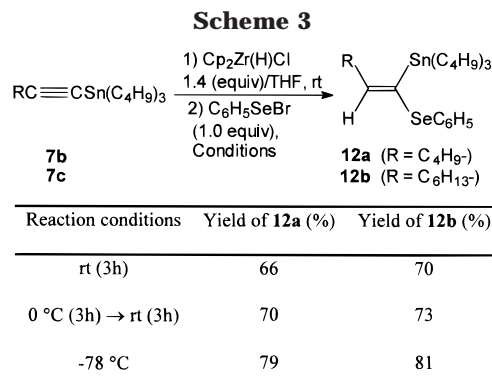
(46) In a recent paper, as a part of the total synthesis of Myxalamide A, Mapp and Heathcock observed the isomerization of conjugated (disubstituted) vinyl iodides during the tin/iodine exchange. These authors employed 1.0 equiv of I$_2$ in CH$_2$Cl$_2$ at room temperature. See Supporting Information in: Mapp, A. K.; Heathcock, C. H. *J. Org. Chem.* **1999**, *64*, 23.

As depicted in Scheme 1, the crude reaction products obtained by reaction of **6a**−**e** with iodine contain the dihalotelluro compounds **9a**−**e**, tributyltin iodide, and the iodine used in excess. These mixtures were initially washed with an aqueous/ethanolic solution of sodium borohydride to remove excess iodine[17j,47] and to transform **9a**−**e** into **4a**−**e**. These transformations were very efficient (at −40 °C); however, the tributyltin iodide was also reduced to the tributyltin hydride as confirmed by the ^{1}H NMR spectrum of the resulting mixture. We observed that compounds **4a**−**e** undergo decomposition in the presence of tributyltin hydride if the mixture is allowed to stay at room temperature; the longer the contact time, the lower the yields obtained. Formation of the tributyltin hydride was avoided by treating the crude product with an aqueous solution of sodium thiosulfate.[17j,48] In this case, the excess iodine and compounds **9a**−**e** were reduced completely while the tributyltin iodide remains intact, which by treatment with potassium fluoride was transformed into the tributyltin fluoride that is insoluble and was retained on top of the column chromatography.

Similar results were obtained in reactions of **6a**−**e** with NBS, but instead of tributyltin iodide, the side product formed was the malodorous solid (tributylstannyl)succinimide (**11**). The (tributylstannyl)succinimide was also retained on top of the column chromatography, and then treatment with potassium fluoride was not necessary in this case (Scheme 2).

It was demonstrated here that the Zr/Te exchange reaction in the intermediates of type **8a**−**e** using 2.0 equiv of butyltellurenyl bromide occurs in a clean manner and with total retention of the configuration. In this context, we must consider the followings: (a) the BuTeBr excess is necessary because of the high halofilicity of the tellurium atom,[22,35−38] that promotes the formation of the dihalogenated compounds as discussed before; (b) the BuTeBr excess is not added to the carbon−carbon double bond of the obtained products **6a**−**e**. During our studies, when the stannylacetylene **7b** (or **7c**) was hydrozirconated at room temperature and the α-zirconated tin vinyl intermediate was subjected to a similar Zr/Se exchange reaction using phenylselenenyl bromide (2.0 equiv), a mixture of products was formed including the expected α-stannylvinyl selenides **12a** (or **12b**). These results were different from the case of the ketene stannyl(telluro) acetals because (a) no dihalogenated compounds at the selenium atom are formed and (b) PhSeBr promotes the addition/elimination reaction on the obtained products **12a** or **12b**. Item b was confirmed because the same mixture of products was obtained after treatment of the pure compounds **12a** or **12b** (obtained as described below) with PhSeBr (1.0 equiv) under similar conditions.

The addition/elimination reaction was almost suppressed by the addition of PhSeBr (2.0 equiv) at −78 °C. Therefore, our studies were directed to improve the obtained results. Consequently, when the hydrozirconation of **7b** was performed by employing 1.0 equiv of Schwartz's reagent and the α-zirconated intermediate was reacted with 1.0 equiv of PhSeBr, only compound **12a** was formed, although in low yield (31%). Treatment of **7c** with 1.2 equiv of ZrCp$_2$(H)Cl followed by reaction with 1.0 equiv of PhSeBr results in the exclusive forma-

Scheme 3

Reaction conditions	Yield of **12a** (%)	Yield of **12b** (%)
rt (3h)	66	70
0 °C (3h) → rt (3h)	70	73
-78 °C	79	81

Scheme 4

tion of **12b** in 50% yield. In these cases, a considerable amount of the starting stannylalkyne and the corresponding selenium free vinylstannane (C$_4$H$_9$CH$_b$=CH$_a$-SnBu$_3$) was also isolated. The vinylstannane was identified by ^{1}H NMR (H$_a$ = d, 6.55 ppm; H$_b$ = dt, 6.17 ppm). These reaction conditions and yields of the obtained products were optimized by performing the hydrozirconation with 1.4 equiv of Cp$_2$Zr(H)Cl at room temperature and the addition of the phenylselenenyl bromide (1.0 equiv) at lower temperatures (0 or −78 °C). The treatment with NaBH$_4$/EtOH was not necessary because no dihalogenated selenium compounds are formed as oppose to the tellurium derivatives case. For instance, compounds **7b** and **7c** were transformed into **12a** and **12b** in 79 and 81% yield, respectively (Scheme 3). With **12a** and **12b** in hand, it was determined that 1.15 equiv of I$_2$ (in THF at 0 °C to room temperature) is sufficient to easily achieve the clean, specific, and complete iodinolysis of the Sn−Csp^2 bond. Indeed, compounds **13a** and **13b** were obtained as only one isomer in 90% and 94% yield, respectively (Scheme 4).

Conclusion

In conclusion, our work describes an efficient method for the stereospecific synthesis of novel ketene stannyl-(chalcogeno) acetals by hydrozirconation of stannylacetylenes. An insight regarding the different reactivity of the tin and tellurium (or selenium) moieties was provided by performing the halogenolysis with iodine and NBS. The chemospecificity of these reactions allowed us to isolate the novel α-halovinyl tellurides **4a**−**e** and **5a**−**e** or α-iodovinyl selenides **13a** and **13b** with retention of the double-bond geometry present in the original ketene stannyl(chalcogeno) acetals **6a**−**e** and **12a** and **12b**. On the basis of the results described here and in the accompanying paper,[49] we can predict that all of the new functionalized vinyl chalcogenides **4a**−**e**, **5a**−**e**, **6a**−**e**, **12a**, **12b**, **13a**, and **13b** obtained here will be of great interest for chemists because they could permit the formation of functionalized vinyllithium intermediates and also the synthesis of heterosubstituted enynes and

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(48) Sabol, J. E.; Kurtz, D. W. *J. Chem. Educ.* **1990**, *67*, 532.

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enediynes. To achieve these goals, chemoselectivity of the Te/Li, Sn/Li, Se/Li, I/Li, and Br/Li exchange reactions in these compounds as the differences on reactivity of cross-coupling reactions of tellurium moiety and other functionalities present in the same molecules remains currently under investigation and will be published in due course.
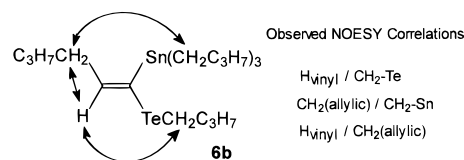
Experimental Section

General Remarks. ^1H and ^{13}C NMR spectra of CDCl$_3$ solutions were recorded with a 300 MHz or a 400 MHz spectrometer as noted. Chemical shifts are expressed as parts per million (ppm) with respect to tetramethylsilane as an internal standard. Mass spectra (EI) were obtained at 70 eV. Elemental analyses were performed at the Instrumental Analysis Center, Chemistry Institute, São Paulo University. Reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Analytical TLC of all reactions was performed using E. M. Merck prepared plates (silica gel 60 F-254 on aluminum). Flash chromatography was performed using 230−400 mesh silica gel. Tetrahydrofuran (THF) was distilled over sodium/benzophenone immediately before use. Dibutyl ditelluride was prepared by the method reported in the literature.[50] The 1-alkynes, butyllithium (2.5 M in hexanes), and bis(cyclopentadienyl)zirconium chlorohydride were purchased from Aldrich Chemical Co. Cp$_2$Zr(H)Cl also was prepared as described in the literature.[27] Stannylacetylenes[51−53] were prepared as previously described in the literature.

Preparation of the Butyltellurenyl Bromide Solution. To a solution of dibutyl ditelluride[50] (0.369 g, 1.0 mmol) in THF (10 mL) cooled at 0 °C was added a solution of bromine (0.16 g, 1.0 mmol) in benzene or CCl$_4$ (10 mL). After stirring for 10 min, the solution of butyltellurenyl bromide was transferred with a syringe to the chalcogenovinylzirconium derivatives as described below.

General Procedure for the Synthesis of Ketene Stannyl(Telluro) Acetals from Stannylacetylenes. To a mixture of Cp$_2$Zr(H)Cl (0.721 g, 2.8 mmol) in THF (10 mL) under nitrogen was added via syringe a solution of the corresponding stannylacetylene (2.0 mmol) in THF (5 mL). The reaction was stirred at room temperature for the time indicated in Table 1. The disappearance of the starting material was confirmed by TLC using hexane as the eluent. The resulting solution was cooled to 0 °C, and a solution of butyltellurenyl bromide (4.0 mmol) prepared separately as described above was transferred via syringe. The stirring was continued for an additional 30 min at 0 °C, and then the mixture was transferred to an Erlenmeyer flask (1 L) and diluted with ethyl acetate (30 mL), water (100 mL), and 95% ethanol (50 mL). Butyl bromide (1.0 mL) and finally NaBH$_4$ (until the mixture turned pale yellow) were added to transform dibutyl ditelluride to the corresponding telluride which is more easily removed by distillation. After this treatment the product was extracted with ethyl acetate (3×) and washed with water (3×). The organic phase was dried over anhydrous MgSO$_4$ and the solvent partially evaporated. After filtration through Celite using hexane as the eluent, the product was concentrated under vacuum. Dibutyl telluride was removed by distillation from the crude product using a Kugelrohr apparatus. Flash column chromatography (hexane) of the residue afforded ketene stannyl(telluro) acetals as yellow liquids.

(*E*)-1-(Butyltelluro)-1-(tributylstannyl)-1-hexene (6b): yield 0.90 g (81%); ^1H NMR (300 MHz) (δ in CDCl$_3$) 0.80−1.0 (m, 21H), 1.3−1.7 (m, 18H), 1.72 (quint, $J = 7.3$, 2H), 2.09 (q, $J = 6.9$ Hz, 2H), 2.70 (t, $J = 7.3$ Hz, 2H), 6.90 (t, $J = 6.9$ Hz, 1H); ^{13}C NMR 11.9, 13.5, 13.7, 14.0, 22.5, 25.3, 27.4, 29.1, 31.9,

Observed NOESY Correlations

H$_{vinyl}$ / CH$_2$-Te

CH$_2$(allylic) / CH$_2$-Sn

H$_{vinyl}$ / CH$_2$(allylic)

6b

33.7, 39.2, 39.4, 109.7, 155.7. Anal. Calcd for C$_{22}$H$_{46}$TeSn: C, 47.45; H, 8.33. Found: C, 47.31; H, 8.36.

General Procedure for the Synthesis of α-Iodovinyl Tellurides from Ketene Stannyl(Telluro) Acetals. To a solution of the appropriate ketene stannyl(telluro) acetal (1.0 mmol) in THF (5 mL) under nitrogen and cooled at 0 °C was added dropwise a solution of iodine (0.54 g, 2.15 mmol) in THF (5 mL). The reaction mixture was stirred at 0 °C for 3 h and for an additional 3 h at room temperature. Then it was transferred to an Erlenmeyer flask and treated with a solution of sodium thiosulfate (3 g/80 mL of H$_2$O) under stirring for 30 min. The dark brown color turned clear yellow, and the organic phase was separated, subsequently treated with a solution of KF·2H$_2$O (2.5 g) in H$_2$O (25 mL), and stirred for an additional 30 min. The mixture was extracted with ethyl acetate and washed with a saturated NH$_4$Cl aqueous solution (3×) and water (3×). The organic phase was dried over anhydrous MgSO$_4$, and after filtration, the solvent was evaporated under reduced pressure, resulting in a mixture of a white precipitate and a yellow residue. The product was immediately purified by column chromatography, using hexane as the eluent.

(*E*)-1-Iodo-1-(butyltelluro)-1-hexene (4b): yield 0.36 g

Observed NOESY Correlations

H$_{vinyl}$ / CH$_2$-Te

H$_{vinyl}$ / CH$_2$(allylic)

4b
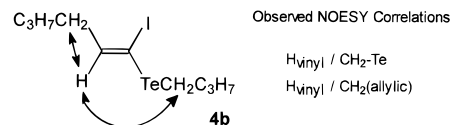
(92%); GC/MS *m/z* 396 (4.00), 81 (96.99), 57 (89.80), 41 (100.00); ^1H NMR (300 MHz) (δ in CDCl$_3$) 0.91 (t, $J = 7.0$ Hz, 3H), 0.94 (t, $J = 7.0$ Hz, 3H), 1.3−1.5 (m, 6H), 1.84 (quint, $J = 7.0$ Hz, 2H), 2.02 (q, $J = 7.0$ Hz, 2H), 2.91 (t, $J = 7.0$ Hz, 2H), 6.61 (t, $J = 7.0$ Hz, 1H); ^{13}C NMR 13.1, 13.5, 13.9, 22.2, 25.1, 29.9, 33.3, 39.7, 49.1, 153.4. Anal. Calcd for C$_{10}$H$_{19}$TeI: C, 30.50; H, 4.86. Found: C, 30.98; H, 4.89.

General Procedure for the Synthesis of α-Bromovinyl Tellurides from Ketene Stannyl(Telluro) Acetals. To a solution of the appropriate ketene stannyl(telluro) acetal (1.0 mmol) in CH$_2$Cl$_2$ (10 mL) cooled at −78 °C (at 0 °C for **5a**) was added dropwise a solution of NBS (0.445 g, 2.5 mmol) in CH$_2$Cl$_2$ (25 mL). The reaction mixture was stirred for 6 h (for **5b−e**) and 12 h (for **5a**). It was transferred to an Erlenmeyer flask and treated with a solution of sodium thiosulfate (3 g/80 mL of H$_2$O) under stirring for 30 min. The solution turned clear yellow, and the mixture was extracted with ethyl acetate and washed with a saturated NH$_4$Cl aqueous solution (3×) and water (3×). The organic phase was dried over anhydrous MgSO$_4$, and after filtration, the solvent was evaporated under reduced pressure. The residue was immediately purified by column chromatography, using hexane as the eluent.

(*E*)-1-Bromo-1-(butyltelluro)ethene (5a): yield 0.13 g (45%); GC/MS *m/z* 294 (34.54), 292 (68.83), 290 (46.90), 57 (100.0); ^1H NMR (300 MHz) (δ in CDCl$_3$) 0.93 (t, $J = 7.0$ Hz, 3H), 1.42 (sext, $J = 7.0$ Hz, 2H), 1.89 (quint, $J = 7.0$ Hz, 2H), 2.95 (t, $J = 7.0$ Hz, 2H), 6.48 (d, $J = 1.5$ Hz, 1H), 6.68 (d, $J = 1.5$ Hz, 1H); ^{13}C NMR 12.6, 13.4, 25.1, 33.5, 125.9, 132.3. Anal. Calcd for C$_6$H$_{11}$TeBr: C, 34.64; H, 5.52. Found: C, 35.02; H, 5.44.

Preparation of Ketene Stannyl(Seleno) Acetals from Stannylacetylenes. To a mixture of Cp$_2$Zr(H)Cl (0.36 g, 1.4 mmol) in THF (5 mL) under nitrogen was added via syringe a solution of the corresponding stannylacetylene (1.0 mmol) in THF (2.5 mL). The reaction was stirred at room temperature for 15 min. The disappearance of the starting material was confirmed by TLC using hexane as the eluent. The resulting solution was cooled to −78 °C, and a solution of phenylsele-

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(51) Bottaro, J. C.; Hanson, R. N.; Seitz, D. E. *J. Org. Chem.* **1981**, *46*, 5221.
(52) Jones, K.; Lappert, M. F. *J. Organomet. Chem.* **1965**, *3*, 295.
(53) Neuman, W. D.; Kleiner, F. G. *Tetrahedron Lett.* **1964**, 3779.

nenyl bromide (1.0 mmol) prepared separately [by the addition of bromine (0.08 g, 0.5 mmol) in CCl_4 (5 mL) to a solution of diphenyl diselenide (0.156 g, 0.5 mmol) in THF, followed by stirring at room temperature for 10 min] was transferred via syringe. The stirring was continued for an additional 30 min at −78 °C, and then the mixture was extracted with ether and washed with water. The organic phase was dried over anhydrous $MgSO_4$ and the solvent evaporated. Flash column chromatography (hexane) of the residue afforded ketene stannyl(seleno) acetals as colorless liquids.

(Z)-1-(Phenylseleno)-1-(tributylstannyl)-1-octene (12b):
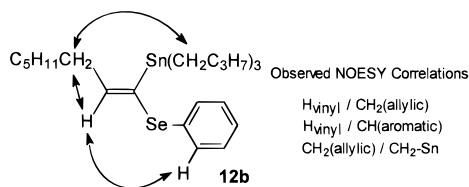
yield 0.45 g (81%); GC/MS *m/z* 558 (1.2), 499 (25.3), 389 (100.0), 275 (43.0); ^{1}H NMR (400 MHz) (δ in CDCl$_3$) 0.80−1.0 (m, 18H), 1.2−1.4 (m, 20H), 2.11 (q, $J = 6.9$ Hz, 2H), 6.72 (t, $J = 7.3$ Hz, 2H), 7.1−7.3 (m, 3H), 7.39 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR 12.6, 14.7, 15.1, 23.7, 28.4, 30.0, 30.2, 30.7, 32.8, 37.8, 127.4, 129.9, 131.4, 132.9, 133.9, 154.0. HRMS. Calcd for $C_{26}H_{46}SeSn$ (M$^+$): 558.1786. Found: 558.1796.

Synthesis of α-Iodovinyl Selenides from Ketene Stannyl(Seleno) Acetals. To a solution of the appropriate ketene stannyl(seleno) acetal (1.0 mmol) in THF (5 mL) under nitrogen and cooled at 0 °C was added dropwise a solution of iodine (0.29 g, 1.15 mmol) in THF (5 mL). The reaction mixture was stirred at 0 °C for 3 h and for an additional 3 h at room temperature. Then it was transferred to an Erlenmeyer flask and treated with a solution of sodium thiosulfate (3 g/80 mL of H_2O) under stirring for 30 min. The dark brown color turned colorless, and the organic phase was separated, subsequently treated with a solution of KF·2H$_2$O (2.5 g) in H$_2$O (25 mL), and stirred for an additional 30 min. The mixture was extracted with ethyl acetate and washed with water (3×). The organic phase was dried over anhydrous MgSO$_4$, and after filtration, the solvent was evaporated under reduced pressure. The product was immediately purified by column chromatography, using hexane as the eluent.

(Z)-1-Iodo-1-(phenylseleno)-1-hexene (13a): yield 0.33 g (90%); GC/MS *m/z* 366 (13.2), 116 (28.5), 84 (100.0); ^{1}H NMR (400 MHz) (δ in CDCl$_3$) 0.92 (t, $J = 7.0$ Hz, 3H), 1.2−1.5 (m, 2H), 1.61 (quint, $J = 7.0$ Hz, 2H), 2.13 (q, $J = 7.0$ Hz, 2H), 6.38 (t, $J = 7.0$ Hz, 1H), 7.33 (m, 3H), 7.49 (m, 2H); ^{13}C NMR 13.9, 22.2, 30.0, 38.1, 79.4, 127.8, 129.3, 131.6, 132.7, 148.6. HRMS. Calcd for $C_{12}H_{15}SeI$ (M$^+$): 365.9383. Found: 365.9401.

Supporting Information Available: Lists of spectral data of compounds **4a,c−e**, **5a,c−e**, **6a,c−e**, **12a**, and **13b**. Copies of the ^{1}H NMR, ^{13}C NMR, and mass spectra of compounds **4a−e**, **5a−e**, **6a−e**, **12a**, **12b**, **13a**, and **13b**. NOESY experiments for compounds **4b**, **6b**, and **12b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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