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Total Control on the Synthesis of Regio and Stereoisomers of Vinylic Tellurides.

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Abstract. Methodologies for the total control on the synthesis of **E**, **Z** or 1,1-dissubstituted vinylic tellurides are described. Tellurobutadienes bearing the butyltellurium moiety at carbon 2 or at carbon 1 with **E** or **Z** configuration at the tellurium containing double bond were also obtained. Addition of diisobutylaluminum butyltellurolate to terminal alkynes resulted in the formation of 1-(butylteluro)- 1-(organyl) ethenes in 45-75 % yield. Al/Te exchange reaction on vinyl alanes with butyl tellurenyl bromide/LiCl furnished the isomers of **E** configuration in 50-60 % yield. Vinylic tellurides of **Z** configuration at the double bond formed were obtained in 30-51 % yield by the hydroalumination of acetylenic tellurides.

Introduction

Vinyl lithium and vinyl copper reagents are important intermediates used for chain elongation in organic synthesis. During the last decades chemists developed different routes of access to this class of reagents[1,2] . The Te/Li exchange reaction which has been known for a long time,[3-7] was first used by Hiiro[8] et al in 1987 to obtain the (**Z**)-stiryl lithium with retention of configuration at the double bond. Other authors extended this reaction to other monoalkenic substrates[9-11] and more recently it was demonstrated by us[12] and others[13-16] that conjugated systems bearing a butyltellurium group undergo transmetalation with absolute retention of the double bond geometry. Although Comasseto[17] stated that the generality of this reaction has been proved, all studies reported to date were developed employing only substrates of **Z** configuration at the double bond bearing the tellurium moiety. The same is observed for the transformation of vinylic tellurium species into vinyl copper reagents[14-16,18] and in other synthetic applications of these compounds.[19-21] This fact is understandable since in spite of the availability of good approaches for the synthesis of (**Z**)-vinyl tellurides, the corresponding **E** isomers were practically unknown and only preparation of the (**E**)-β-styryl butyl telluride[22] was described before 1994. The synthesis of (**E**)-1-phenyltelluro-2-arylethenes *via* phenyltelluro phosphonates[23] and of the (**E**)-1-(butyltelluro)butadiene by a Wittig reaction,[13] have been described recently. The Zr/Te transmetalation on (**E**)-vinyl zirconates with C_6H_5TeI was reported by Korean authors[24] and we report our independent preparation of (**E**)-vinylic tellurides using C_4H_9TeBr in similar reactions.[25]

Similarly, synthesis of **Z** isomers with an alkyl group linked at carbon 2 of the double bond has serious limitations. Sodium tellurolate addition to alkyl acetylenes results in a mixture of isomers (1,2 (**Z**) and 1,1-disubstituted) in very poor yields that are difficult to separate[10,26]. Other existing routes to obtain the vinylic tellurides bearing an alkyl group at a Csp^2 have employed vinyl Grignard reagents, but in this case no control of stereochemistry was made and only few examples were described because of the low availability of alkyl vinyl bromides. The two known 1,1-disubstituted vinyl tellurides were obtained using the last routes.[11,22]

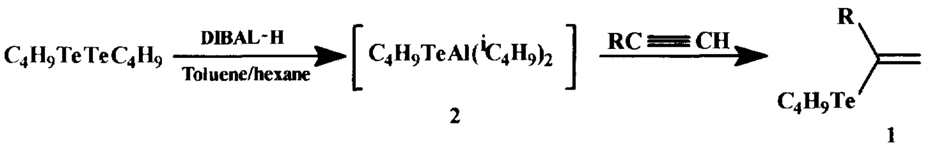
Keeping in mind all the limitations discussed above, and our great interest in the synthetic applications of intermediates with a Csp^2 bearing a butyl tellurium group, we developed several methodologies to permit total control for the synthesis of each E; **Z**; 1,1-disubstituted or acyclic trisubstituted (entry 6; Table 2) regio and stereoisomers. In this paper we report our results employing different reactions with alkynes, DIBAL-H and electrophilic or nucleophilic tellurium species that permit this control.

Results and discussion

1-(Butyltelluro)-1-(organyl) ethenes. The 1-(butyltelluro)-1-(organyl) ethenes **1** were obtained by the aluminotelluration of aliphatic or aromatic substituted terminal alkynes, followed by aqueous quenching. Diisobutylaluminium butyltellurolate **2** (generated by the addition of DIBAL-H in toluene to the dibutylditelluride in hexane) undergoes regiospecific addition to the triple bond, affording the isomer with the tellurium moiety attached at the internal carbon (eq. 1; Table 1). In all cases no trace amounts of other regio-isomeric products could be detected by the analytical methods employed (^1H NMR, ^{13}C NMR, CG/MS).

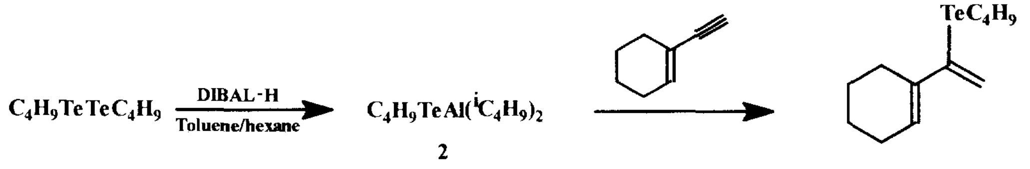
The reaction is performed at reflux for 4 hours and using excess of the terminal acetylene (3.0 equivalents). No formation of products was observed using equimolar amounts of aluminum butyltellurolate and alkyne or with 3 equivalents of **2** at 0°C. In contrast, Sn-,[27] and Si-,[28] based metalloalumination of 1-alkynes requires a 3-fold excess of the organometallic reagent employed to achieve a high alkyne conversion.

In the present telluroalumination the use of catalysts is not required, while other known metallometalations of 1-alkynes are reported to be very slow without added catalysts, such as Cu^+ or Pd°, that improve yields and regiochemical bias.[28,29]



(1)

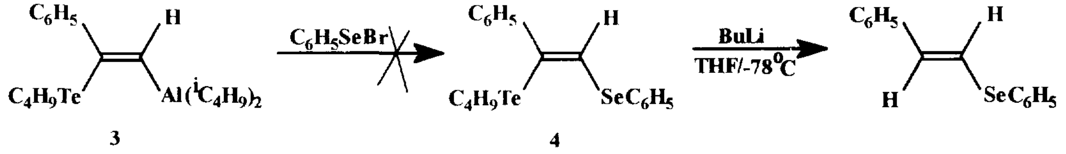
Regiochemistry of the obtained product **1** is contrary to that observed in the product of reaction of sodium butyltellurolate with 1-aryl acetylenes that produces exclusively the isomer of **Z** configuration at the double bond formed as the result of an *anti*-addition.[10] Another interesting contrast is that aluminotelluration regiospecificity is general, including 1-alkyl acetylenes (entries 1, 2, 3 and 4; Table 1), while hydrotelluration of this type of alkynes, using sodium butyltellurolate results in mixtures of regio isomers.[10,26] 2-Butyltelluro-1,3-butadienes were also obtained when the same aluminotelluration reaction was applied to conjugated enynes with the terminal triple bond (eq. 2, entries 8 and 9; Table 1). On the other hand, reaction of internal alkynes (e.g. 3-hexyne) fails completely. No aluminotelluration reaction occurs also with terminal alkynes when performed by slow addition of 1-alkynes to **2** at low temperatures (-30°C or -78°C), contrary to the stannylalumination,[27] where high alkyne consumption and minimal formation of side-products were observed at -30°C.



(2)

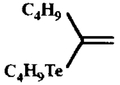
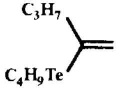
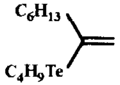
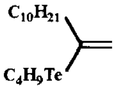
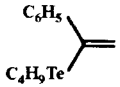
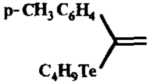
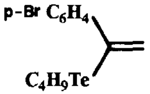
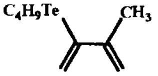
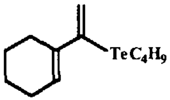
To establish the stereochemistry for aluminotelluration of alkynes, we attempted to trap the vinyl alane intermediate **3** by reaction with phenyl selenenyl bromide to give the 1-phenyl-1-butyltelluro-2-phenylseleno ethene **4** (Scheme 1). Further removal of the tellurium moiety by the Te/Li exchange reaction and analysis of stereochemistry of the vinylic selenide obtained could inform us if the aluminotelluration of 1-alkynes with **2** involves a *syn* or *anti*-addition of Al-Te species. However, capturing **3** was not possible in this way and **4** was not formed (Scheme 1).

Scheme 1



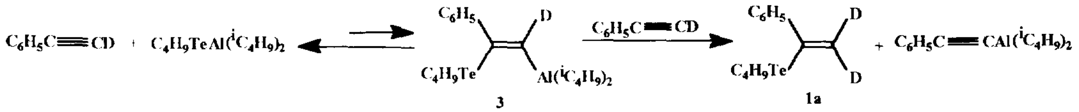
On the basis of discussed facts and the observation that 3.0 equivalents of terminal alkynes are necessary for the reaction to occur with good yields, we believe that the addition step is reversible and highly favorable to the reactants. Then, no detectable product formation was observed when equimolar amounts of acetylene and **2** were used. Excess of 1-alkyne provides a proton for the intermediates of type **3**, promoting the protonolysis before the reaction work-up to give **1**. The last step is irreversible, shifting the equilibrium to product formation. To confirm this assumption, we performed the reaction of **2** with 3.0 equivalents of deuterated phenyl acetylene under reflux for 4 hours (Scheme 2) and then quenched the products by water. After usual work-up and purification by column chromatography, d_2-1-butyltelluro-1-phenyl ethene (d_2 ~ 95 %) **1a** was obtained in 73 % yield (Scheme 2). This evidence suggests that the terminal alkyne functions as the proton donor. It is worthy to mention here that excess of the alkyne can be recovered by distillation after aqueous work-up.

Table 1. 1-(Butyltelluro)-1-(organyl)ethenes obtained.

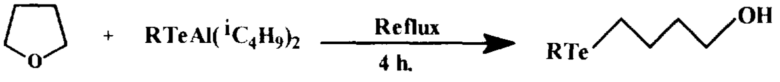
Entry	Product	Yield (%)[a]	anal. found (calcd.)		^{1}H NMR, ppm (J, Hz; TMS internal)
			H	C	
1		65	7.32 (7.40	44.43 44.44)	0.9(t, J=7 Hz, 6H) 1.0-2.0(m, 8H) 2.30(t, J=7 Hz, 2H) 2.75(t, J= 7 Hz, 2H) 5.35(s, 1H) 5.84(t, J~1.3 Hz, 1H)
2		49	7.00 (7.15	42.38 42.59)	0.85(t, J= 7Hz, 6H) 1.1-2.0(m, 6H) 2.32(t, J=7 Hz, 2H) 2.78(t, J= 7 Hz, 2H) 5.38(s, 1H) 5.88(t, J~1.3 Hz, 1H)
3		53	7.99 (8.11	48.66 48.71)	0.85(t, J=7 Hz, 3H) 0.92(t, J=7 Hz, 3H) 1.1-2.0(m, 12H) 2.30(t, J=7 Hz, 2H) 2.75(t, J=7 Hz, 2H) 5.35(s, 1H) 5.87(t, J~1.3 Hz, 1H)
4		55	8,98 (9.16	54.85 54.59)	0.88(t, J=7 Hz, 3H) 0.91(t, J=7 Hz, 3H) 1.1-2.0(m, 20H) 2.30(t, J=7 Hz, 2H) 2.73(t, J=7 Hz, 2H) 5.32(s, 1H) 5.82(t, J~1.0 Hz, 1H)
5		75	5.54 (5.60	50.11 50.07)	0.82(t, J=7 Hz, 3H) 1.1-1.9(m, 4H) 2.63(t, J=7 Hz, 2H) 5.7(s, 1H) 6.15(s, 1H) 7.1-7.6(m, 5H)
6		63	6.11 (6.01	51.60 51.72)	0.86(t, J=7 Hz, 3H) 1.1-2.0(m, 4H) 2.3(s, 3H) 2.68(t, J=7 Hz, 2H) 5.67(s, 1H) 6.13(s, 1H) 7.1(d, J=8 Hz, 2H) 7.40(d, J=8 Hz, 2H)
7		45	4.26 (4.11	39.14 39.14)	0.9(t, J=7 Hz, 3H) 1.2-2.1(m, 4H) 2.78(t, J=7 Hz, 2H) 5.73(s, 1H) 6.17(s, 1H) 7.38(m, 5H)
8		47	6.34 (6.29	42.39 42.51)	0.9(t, J=7 Hz, 3H) 1.1-1.9(m, 4H) 2.0 (t, J~1,3 Hz, 3H) 2.73(t, J=7 Hz, 2H) 5.1(q, J~1.0 Hz, 1H) 5.25(s, 1H) 5.65(s, 1H) 6.15(s, 1H)
9		69	6.93 (6.91	49.72 49.38)	0.89(t, J=7 Hz, 3H) 1.1-2.4(m, 12H) 2.72(t, J=7 Hz, 2H) 5.50(s, 1H) 6.04(s, 2H)

[a] Isolated Yields.

Scheme 2



Attempts to use the diisobutylaluminum butyl (or phenyl)tellurolate anion generated in THF as described previously for the preparation of $({}^{i}C_4H_9)_2AlTeC_6H_5$[30,31] or $({}^{i}C_4H_9)_2AlTe{}^{n}C_4H_9$[32] were unsuccessful. Under our conditions (reflux), the nucleophilic attack of tellurolate anion to the solvent (THF) was favorable, resulting in the exclusive formation of the 4-butyltelluro-1-butanol **5a** or the 4-phenyltelluro-1-butanol **5b** rather than vinylic telluride formation. When the reaction was performed in the absence of terminal alkynes, compounds **5a** and **5b** were obtained in 72% and 67 % yield respectively (eq.3). Analogous nucleophilic ring opening of oxiranes and the reactivity of diisobutylaluminum tellurolate anions toward others functional groups were previously described using THF as solvent, however these reactions were performed at room or lower temperatures.[30-32]

 (3)

5a $R = C_4H_9$- 72 % yield
5b $R = C_6H_5$- 67 % yield

Synthesis of (E)-1-(butyltelluro)-2-(organyl)ethenes. Vinyl alane intermediates produced by hydroalumination of acetylenes with DIBAL-H have been shown to react with different electrophiles to give other vinylic elemental derivatives, such as vinyl stannanes[33], vinyl halides[34], and others.[35] The vinyl alanes of E configuration were obtained by treatment of a solution of the terminal alkyne in hexane at 0°C with DIBAL-H in toluene followed by reflux for 3h. Pursuing the development of a convenient and general access to vinylic tellurides of E configuration, we set out to examine the Al/Te transmetalation on the (E)-vinyl alanes with butyltellurenyl bromide, facilitated by LiCl. We now report that this process occurs with total retention of configuration, affording exclusively the alkyl (or aryl) butyltelluro ethenes and the 2-butyltelluro-1,3-butadienes with **E** stereochemistry at the newly formed double bond (Scheme 3; Table 2).

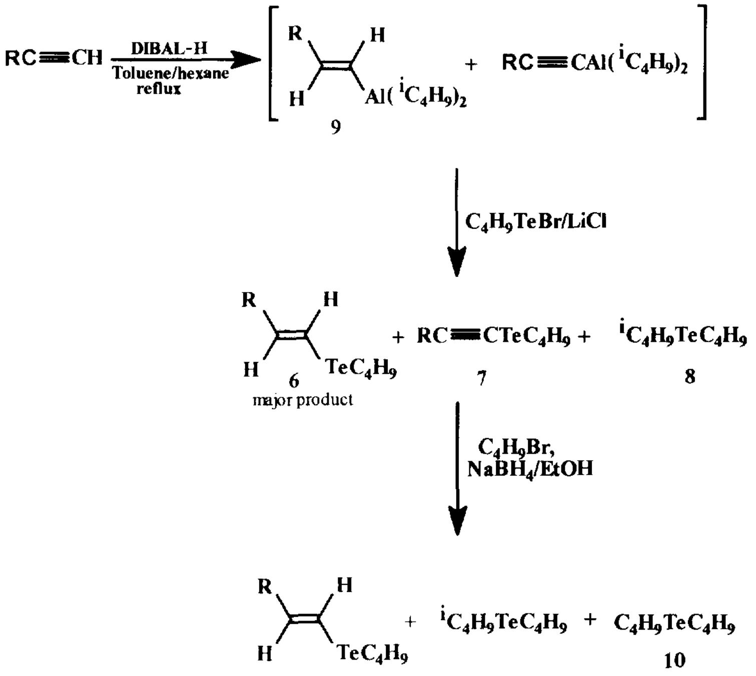
Together with the formation of vinylic telluride **6** as the major product, two side-reactions were observed. The corresponding butyltelluro acetylenes **7** and the butyl isobutyl telluride **8** were obtained in all cases. The routes to these side-products could involve 1) capture of an aluminum acetylide intermediate[35] by the butyltellurenyl bromide and 2) the transmetalation at Csp^3 in **9**.[35]

It has been reported previously that vinyl alanes obtained by hydroalumination of terminal alkynes were contaminated with small amounts of $RC{\equiv}CAlR'_2$ formed from metalation of terminal alkynes by aluminum alkyls[36] or by vinyl alanes.[37]

The addition of dry LiCl to the solution of butyltellurenyl bromide before use is important since in the absence of the lithium salt, the Al/Te exchange reaction does not occur. The last reaction is also very sensitive to the solvents used and the best results were obtained with a mixture of hexane/toluene for the hydroalumination and THF/benzene to generate the butyltellurenyl bromide.[22] Purification of the solvents immediately before use in this reaction was obligatory. The use of stocked solvents even over sodium causes an increase in formation of butyltelluro acetylenes **7** as in the case of phenylacetylene where the corresponding telluroacetylene was obtained free of the vinylic analogue (entry 7).

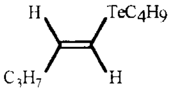
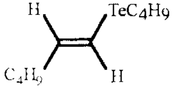
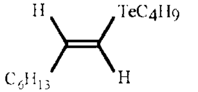
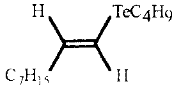
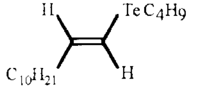
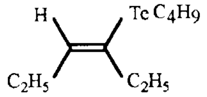
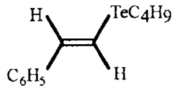
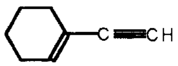
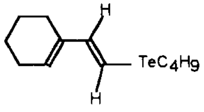
While **7** could be separated easily by column chromatography, **8** shows in several solvents or mixtures of solvents the same retention factor (R_f) as most of the (**E**)-vinylic tellurides obtained. Considering our interest in obtaining analytically pure samples of the last compounds, the butyltelluro acetylenes and the dibutylditelluride (formed from the remaining butyl tellurenyl bromide) present in the crude reaction mixture were transformed into the dibutyltellurides by reaction with bromobutane and sodium borohydride in ethanol at room temperature[38] (Scheme 3). Then, from the resulting mixture, dibutyltellurides (**8** and **10**) were removed by horizontal distillation on a Kugelrohr apparatus. The residue contains the (E)-vinylic telluride that was purified by column chromatography.

Scheme 3



Only the butyltelluro phenylacetylene was obtained in pure form after separation by flash chromatography in 32% yield. Other analogous compounds **7** formed were not quantified (for entries 1-6 and 8), but transformed into dialkyl derivatives as described above to simplify the isolation of **6**.

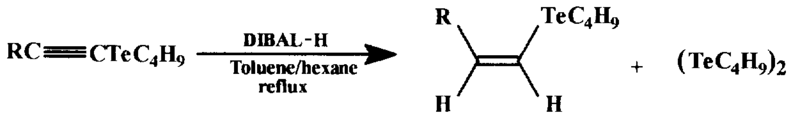
Table 2. (E)-1-(butyltelluro)-2-(organyl)ethenes obtained by Al/Te exchange reaction.

Entry	Alkyne	PRODUCT	Yield (%)[a]	Anal. Found (calcd.) H	Anal. Found (calcd.) C	^{1}H NMR, ppm (J = Hz; TMS internal)
1	$C_3H_7C\equiv CH$		54	7.15 (7.09	42.72 42.58)	0.9(t, J=7 Hz, 6H) 1.1-2.3(m, 8H) 2.68(t, J=7 Hz, 2H) 6.18(dt, J=16 Hz, J=5.6 Hz, 1H) 6.60(dt, J=16 Hz, J~0.5 Hz, 1H)
2	$C_4H_9C\equiv CH$		52	7.62 (7.47	44.72 44.84)	0.89(t, J=7 Hz, 3H) 0.9(t, J=7 Hz, 3H) 1.1-2.3(m, 10H) 2.68(t, J=7 Hz, 2H) 6.16(dt, J=16Hz, J=5.6 Hz, 1H) 6.60(dt, J=16 Hz, J~0.5Hz, 1H)
3	$C_6H_{13}C\equiv CH$		56	8.04 (8.11	48.44 48.71)	0.86(t, J=7 Hz, 3H) 0.90(t, J=7 Hz, 3H) 1.1-2.0(m, 12 H) 2.10(t, J=7 Hz, 2H) 2.69(t, J=7 Hz, 2H) 6.18(dt, J=16 Hz, J=5.6 Hz, 1H) 6.58(d, J=16 Hz, 1H)
4	$C_7H_{15}C\equiv CH$		50	8.30 (8.39	50.11 50.38)	0.86(t, J=7 Hz, 3H) 0.90(t, J=7 Hz, 3H) 1.1-2.0(m, 14H) 2.09(t, J=7 Hz, 2H) 2.65(t, J=7 Hz, 2H) 6.18(dt, J=16 Hz, J=5.6 Hz, 1H) 6.56(d, J=16 Hz, 1H)
5	$C_{10}H_{21}C\equiv CH$		56	9.33 (9.16	55.07 54.59)	0.95(t, J=7 Hz, 6H) 1.2-2.3(m, 22H) 2.62(t, J=7 Hz, 2H) 6.10(dt, J=16 Hz, J=5.6 Hz,1H) 6.50(d, J=16 Hz, 1H)
6	$C_2H_5C\equiv CC_2H_5$		60	7.55 (7.87	45.31 44.67)	0.8-1.1 (m, 9H) 1.2-2.6 (m, 8H) 2.70 (t, J=7 Hz, 2H) 5.98 (t, J=7 Hz, 1H)
7	$C_6H_5C\equiv CH$		56	6.78 (6.91	49.46 49.31)	0.91(t, J=7 Hz, 3H) 1.40(sext., J=7 Hz, 2H) 1.82(quint., J=7 Hz, 2H) 2.80(t, J=7 Hz, 2H) 6.98(d, J=16 Hz, 1H) 7.30(s, 5H) 7.48(d, J=16 Hz, 1H)
8			55	ref. 10		0.95(t, J=7 Hz, 3H) 1.1-1.9(m, 4H) 2.0-2.2(m, 8H) 2.72(t, J=7 Hz, 2H) 5.6(m, 1H) 6.68(s, 2H)

[a] Isolated Yields.

Synthesis of (Z)-1-(butyltelluro)-2-(organyl)ethenes. Acetylenic tellurides undergo easy Te-spC bond cleavage by reaction with reducing agents such as $LiAlH_4$ in tetrahydrofuran, $NaBH_4$ in ethanol, and hydrazine-sodium hydroxide (diimide), giving the tellurium-free acetylene and the diorganyl ditelluride.[38] Reduction with $NaBH_4$ and $LiAlH_4$ occurs through attack of hydride at the tellurium atom.[38] Tellurolate anions are intermediates in these reactions, as confirmed by performing the reaction under a deoxygenated atmosphere, at reflux. Under the last conditions, nucleophilic addition of the tellurolate anion to phenyl acetylene occurs, and vinylic tellurides of *cis* configuration were obtained. However, this reaction occurs only when $NaBH_4$/ethanol or diimide/ethanol is used because a protic solvent is necessary to capture the intermediate vinyl anion. The last reaction was observed only with phenyl acetylene derivatives because of the low reactivity of alkyl acetylenes.[38] As discussed before, reaction of tellurolate anions with alkyl acetylenes can occur but a mixture of regioisomers is obtained and yields are very low.[10,26]

The ease with which tellurium is attacked by nucleophiles and the specificity with which the tellurium-sp carbon bond is cleaved indicates that this bond is highly polarized. However, in view of our interest in developing a general approach to (**Z**)-vinylic tellurides bearing alkyl or aryl groups directly bonded to Sp^2 carbon, we have studied here the chemical behavior of telluro alkynes with aryl or alkyl groups attached to the triple bond when treated with DIBAL-H in toluene/hexane (eq. 4). Our studies involved the addition of a solution of DIBAL-H in toluene to butyltelluro hexyne, followed by aqueous work-up. In this case the (**Z**)-1-butyltelluro-1-hexene was obtained in 51 % yield (entry 1; Table 3).



(4)

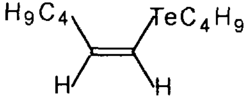
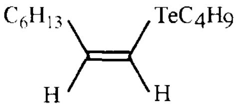
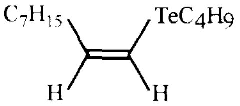
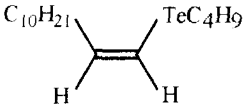
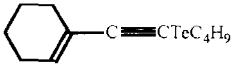
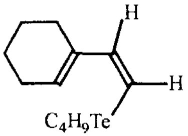
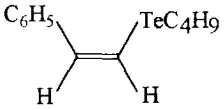
Fast addition of DIBAL-H was performed at 0°C and the pale yellow solution of the telluroacetylene turned red due to the formation of dibutyl ditelluride as a side product, resulting from the partial cleavage of the spC-Te bond. Reactions were monitored by TLC and the complete disappearance of the starting telluroalkynes was observed in all cases after a period of 2 hours under reflux. The (**Z**)-1-(butyltelluro)-2-(alkyl or aryl)ethenes were obtained in moderated yield (Table 3). No formation of other isomeric products was detected by the analytical methods employed (^1H NMR, ^{13}C NMR, CG/MS). We believe that in the present case the spC-Te bond cleavage and the direct *syn* hydroalumination of the triple bond are competitive reactions.

Reaction of butyltelluro phenyl acetylene results in formation of the corresponding (**Z**)-1-butyltelluro-2-phenyl ethene in only 30% yield (entry 6, Table 3) because the cleavage of the spC-Te bond is easier than in other cases (entries 1 to 5) and large amounts of dibutyl ditelluride are formed.

Conclusion

As stated above, we have developed three different methodologies that permits the total control on the regio and stereochemistry of vinylic tellurides synthesized, included the first general approach to the 1,1-disubstituted isomers. Further studies of synthetic applications of vinylic tellurides prepared here to obtain α-methylene and γ-butyro lactones are now in progress in our laboratory.

Table 3. - (Z)-1-(tellurobutyl)-2-(organyl)ethenes prepared.

Entry	ALKYNE	PRODUCT	Yield (%)[a]	Anal. found(calcd.) H	Anal. found(calcd.) C	^{1}H NMR, ppm (J, Hz; TMS internal)
1	$C_4H_9C\equiv CTeC_4H_9$		51	**7.24** **(7.40**	**44.33** **44.44)**	0.87(t, J=7 Hz, 3H) 0.91(t, J=7 Hz, 3H) 1.1-2.2(m, 10H) 2.65(t, J=8 Hz, 2H) 6.11(dt, J=9.6 Hz, J=6.6 Hz, 1H) 6.55(dt, J=9.3 Hz, J~0.5Hz, 1H)
2	$C_6H_{13}C\equiv CTeC_4H_9$		51	**8.01** **(8.13**	**49.12** **48.81)**	0.88(t, J=7 Hz, 3H) 0.91(t, J=7 Hz, 3H) 1.1-2.2(m, 14H) 2.68(t, J=7 Hz, 2H) 6.12(dt, J=9.3 Hz, J=6.7 Hz, 1H) 6.56(dt, J=9.3 Hz, J~0.5 Hz, 1H)
3	$C_7H_{15}C\equiv CTeC_4H_9$		50	**8.16** **(8.46**	**50.73** **50.38)**	0.8-1.1(m, 6H) 1.1-2.2(m, 16H) 2.62 (t, J=7 Hz, 2H) 6.10(dt, J=9.33 Hz, J=6.66 Hz, 1H) 6.48(d, J=9.33 Hz, 1H)
4	$C_{10}H_{21}C\equiv CTeC_4H_9$		42	**8.93** **(9.16**	**54.11** **54.59)**	0.88(t, J=6.66 Hz, 3H) 0.92(t, J=6.66 Hz, 3H) 1.30(s, 16H) 1.5-2.3(m, 6H) 2.76(t, J=7 Hz, 2H) 6.15(dt, J=9.33 Hz, J=6.6 Hz, 1H) 6.55(dt, J=9.33 Hz, J~0.5 Hz, 1H)
5			47	**6.97** **(6.91**	**49.56** **49.38)**	0.95(t, J=6.6 Hz, 3H) 1.1-2.3(m, 11H) 2.72(t, J=6.6 Hz, 2H) 5.3(m, 1H) 6.45(d, J=10.7 Hz, 1H) 6.76(d, J=10.7 Hz, 1H)
6	$C_6H_5C\equiv CTeC_4H_9$		30	**ref. 38**		0.85(t, J=6.7 Hz, 3H) 1.32(sext., J=6.7 Hz, 2H) 1.75(quint., J=6.7 Hz, 2H) 2.62(t, J=7 Hz, 2H) 6.90(d, J=10.6 Hz, 1H) 7.25(s, 5H) 7.35(d, J=10.6 Hz, 1H)

[a] Isolated Yields.

Experimental

General remarks. ^{1}H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded with a Brucker AC 80 (80 and 20.15 MHz, respectively) spectrometer. Chemical shifts are expressed as parts per million (ppm) with respect to tetramethylsilane as an internal standard. IR spectra were obtained on neat samples and recorded with a Perkin-Elmer model 1600 spectrometer. Mass spectra (EI) were obtained at 70 eV with a Hewlett Packard EM/CG HP-5988A spectrometer. Elemental analyses were performed at the Instrumental Analysis Center of the Chemistry Institute, São Paulo University. Reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Merck silica gel (230-400 mesh) was used for flash chromatography. All solvents used were distilled from sodium immediately prior to use. The alkynes, n-butyllithium (2,5 M in hexanes), LiCl and DIBAL-H (pure or 1,0 M in toluene) were purchased from Aldrich Chemical Co., Inc. Dibutylditelluride, [39] and acetylenic tellurides[38] were prepared by the procedures reported in the literature.

General procedure for the synthesis of 1-(tellurobutyl)-1-(organyl)-ethenes. To a solution of dibutyl ditelluride (0.738 g; 2.0 mmol) in dry hexane (4.0 mL) contained in a two neck round bottomed flask, DIBAL-H (4.0 mL, 4.0 mmol, sol. 1.0 M in toluene) was added and the mixture refluxed. The corresponding alkyne (12.0 mmol) was added at once to the resulting yellow solution and the reaction mixture refluxed for 4 hours. After this time the reaction was cooled to 0 °C, water was added (4.0 mL) and the product extracted with hexane (3 x 50 mL) and ethyl acetate (3x 50 mL). The organic phases were dried over anhydrous $MgSO_4$ and the solvents evaporated under reduced pressure. The alkyl tellurium compounds were removed by distillation using a Kugelrohr apparatus. The residue is the vinylic telluride which was purified by flash chromatography using hexane as eluent. Yields are listed in Table 1.

General procedure for the synthesis of (Z)-1-(tellurobutyl)-2-(organyl) ethenes. To a 25 mL round bottomed flask, containing a solution of the corresponding butyltelluro alkyne (2.0 mmol) in dry hexane (2.0 mL), DIBAL-H (2.0 mmol, 2.0mL, sol. 1M in toluene) was added at once. The reaction mixture was refluxed for 2 hours, then cooled to room temperature and water added (2.0 mL). The product was extracted with hexane (3 x 50 mL) and ethyl acetate (2 x 50 mL). The organics were washed with water (3 x 50 mL), dried over anhydrous $MgSO_4$ and the solvents evaporated. The product was purified by column chromatography using hexane as eluent for entries 5 and 6 (Table 3) and as above for others. Yields are listed in table 3.

General procedure for the synthesis of (E)-1-(tellurobutyl)-2-(organyl)ethenes. To a 25 mL round-bottomed flask, containing a solution of the corresponding alkyne (4.0 mmol) in dry hexane (4.0 mL) at 0 °C, DIBAL-H (4.0 mL, 4.0 mmol, 1.0 M in toluene) was added at once. The mixture was slowly warmed for 45 minutes and then refluxed for 3 hours. The reaction was cooled to room temperature and dry hexane (8.0 mL) and dry toluene (8.0 mL) were added.

Concurrently, the butyltellurenyl bromide was obtained by the addition of a solution of bromine (0.16g; 2.0 mmol) in benzene (~10 mL) to the solution of dibutylditelluride (0.738 g; 2.0 mmol) in hexane cooled at 0 °C under a nitrogen atmosphere. The mixture was stirred at 0 °C for 10 minutes, then LiCl (0.196 g; 4.2 mmol) was added, the dark solution turned clear red and stirring was continued until all LiCl was dissolved (10 min.). The resulting solution was transferred to the flask containing the vinyl alane. The reaction was stirred for 2 hours at room temperature and then a mixture of ice and water (~ 60 mL) was added. The solids were filtered and the products extracted with hexane (3 x 70 mL) and ethyl acetate (2 x 70 mL). The organic layers were combined and after drying over anhydrous $MgSO_4$, the solvents were removed under reduced pressure. To obtain analytically pure samples of the vinylic tellurides, the crude mixture was dissolved in 95% ethanol (20 mL) and $NaBH_4$ (~ 0.18 g) was added. The resulting yellow solution was stirred for 10 minutes, extracted with petroleum ether (2 x 70 mL), and washed with water (5 x 70 mL). After drying the organic phase over anhydrous $MgSO_4$, the solvent was removed under reduced pressure and the residue distilled in a Kugelrohr apparatus to remove the alkyl tellurides. The residue is the vinylic telluride that was purified by column chromatography using hexane as eluent. Yields are listed in Table 2.

1-Butyltelluro-2-butanol 5a. To a solution of dibutyl ditelluride (0.738 g; 2.0 mmol) in THF (3 mL) contained in a two neck round bottomed flask, DIBAL-H was added until the dark red color turned pale yellow (~4.4 mL; 4.4 mmol; sol. 1.0 M in hexane). The reaction was stirred under reflux for 1 hour and stand to reach room temperature, then a saturated solution of NH_4Cl was added (5 mL). The solids formed were filtered and washed with water and ethyl acetate (~100 mL). The organic layer was washed with water (3 x 50 mL) and dried over anhydrous $MgSO_4$ and solvent evaporated under reduced pressure. The residue was purified by flash chromatography using hexane to remove some remaining dibutyl ditelluride, and ethyl acetate to elute the pure compound **5a**. Yield: 0.742g (72%). ^1H NMR δ ($CDCl_3$) 0.95 (t, J=7 Hz, 3H) 1.1-2.1 (m, 10H) 2.63 (t, J=7 Hz, 2H) 3.51 (t, J=7 Hz, 2H) 3.83 (broad s., 1H). MS m/z 258 (M^+), 57 (100.00).

1-Phenyltelluro-2-butanol 5b.The same procedure as above was followed using diphenyl ditelluride (0.299g, 1.0 mmol). Compound **5b** was obtained as a yellow oil. 0.372g (67 %). ^1H NMR δ ($CDCl_3$) 1.2-2.2 (m, 4H), 2.76 (s, 1H), 2.86 (t, J=7 Hz, 2H), 3.50 (t, J=7 Hz, 2H), 7.0-7.3 (m, 3H), 7.4-7.8 (m, 2H). MS m/z 280 (M^+), 77 (100.00).

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