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(1*Z*,3*Z*)-Buta-1,3-Dienyl-1-Lithium Species and Substituted Tellurophenes by Te/Li exchange on (1*Z*,3*Z*)-Butyltelluro-1,3-Butadienes and (1*Z*,3*Z*)-1,4-bis(Butyltelluro)-1,3-Butadienes.

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Abstract. (1*Z*,3*Z*)-1-Butyltelluro-1,3-butadienes **8, 9** and **12** obtained by the hydrotelluration of but-1-en-3-ynes **1, 2** and **5** were transformed into the corresponding buta-1,3-dienyl-1-lithium by reaction with n-BuLi. 1,3-Butadienes **14**, **15**, **17-20** were obtained with retention of the double bond geometry by reaction of the butadienyllithium intermediates with electrophiles. The butadienyllithium **13** obtained by the Te/Li exchange reaction in the (1*Z*,3*Z*)-1-Butyltelluro-4-methoxy-1,3-Butadiene **8** was reacted with benzaldehyde to form the corresponding alcohol **15** with total retention of configuration, that undergoes hydrolysis resulting into the (*E,E*)-5-phenyl-2,3-pentadien-1-al **16**. Hydrotelluration of the 1-butyltellurobut-1-en-3-yne **3** permits the synthesis of the (1*Z*,3*Z*)-1,4-bis(butyltelluro)-1,3-butadiene **10** which undergoes cyclization, leading to substituted tellurophenes **24, 25, 27-29** *via* a sequential Csp^2-Te and Csp^3-Te bonds cleavage on reaction with n-BuLi followed by addition of electrophiles. © 1997 Elsevier Science Ltd.

INTRODUCTION

Dienic conjugated systems construction has received considerable attention by chemists, since it constitutes a fundamental structural feature of many insect pheromones[1] and other biologically active compounds or are largely used in Diels-Alder reactions.[2] In this way, several methods have been developed for the stereoselective synthesis of conjugated dienes that permits the preparation of different isomers in a high degree of purity. However, methods that permit the access to the *E,E* isomers are the more developed for use in Diels-Alder condensation reactions, where dienes must adopt the s-*cis* configuration. Dienes of *E,Z* or *Z,Z* stereo chemistry are available by a limited number of methodologies and they are less thermodynamically stable than *E,E* isomers. Some of the most useful approaches to 1,3-butadienes involved the cross coupling reaction of vinyl halides[3] with vinyl organometallics such as vinyl cuprates,[3e] vinyl Grignard[3f] reagents, vinyl zincates[3c,d] and others, the Horner-Wittig type olefination reaction,[4] retro Diels-Alder reaction of mono or di-substituted sulfolenes[5,6] and the selective hydro[3d,7] or carbo[8] metallation of alkynes and the electrocyclic ring opening of cyclobutenes.[9]

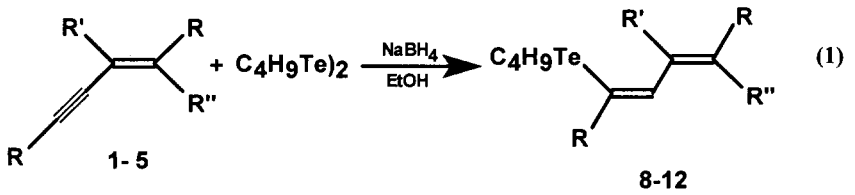
It is known that sulfur atom produces an increment on reactivity[5b,5c] of the diene and permits the control of regiochemistry in products of Diels-Alder reaction.[5b,6] Sulfur containing dienes were also used in synthesis of insect pheromones.[8a] The use of 2-phenylseleno-1,3-butadiene generated *in situ* in a regioselective Diels-Alder reaction using unsymmetrical dienophiles[5b] was described, and other selenobutadienes were used as precursors of cyclopentanone ring systems such as dehydrojasmone.[10] In spite of this, telluro containing dienes are scarcely known.[11-13] In a previous paper, the hydrotelluration of ***E*** or ***Z***-1,3-enynes with the stereospecific reduction of the triple bond was reported.[12] This reaction permits the access to (***Z,E***) and (***Z,Z***)-1-(organyltelluro)-1,3-butadienes respectively. We also described the Li/Te exchange reaction on mono-olefinic tellurides[12] and tellurobutenynes[14] to prepare vinyllithium species of defined configuration. Other authors described the ready availability of vinyllithium reagents[15] and more recently Mo and Huang[13a] obtained butadienyllithium intermediates by the Te/Li exchange reaction on the 1-butyltellurobutadiene of ***E*** and ***Z*** configuration, which were obtained *via* Wittig reaction. These Te/Li exchange reactions constitute a very interesting method for generating organolithium compounds to be used *in situ* since reactions occurs rapidly, stereospecifically and the diorganyl telluride formed as a side product can be easily separated from products by chromatography on silica gel. Luppold et al[16] obtained a butadienyl di-lithium derivative by the ring cleavage of 2,5-diphenyltellurophene using BuLi/TMEDA reagent in ether, to give (***E,E***)-1,4-diphenyl-1,3-butadiene upon hydrolysis or the (***E,E***)-1,4-diphenyl-2,4-hexadiene after alkylation with methyl iodide.

We now report our results on the synthesis of several highly functionalized (***Z,Z***)-telluro-1,3-butadienes bearing a butyltelluro moiety at 1-position of the butadienylic system, on the clean and easy Te/Li exchange reaction of these compounds to generate butadienyl lithium species and on the further transformations of the lithium intermediates so formed. We also report the preparation of (***Z,Z***)-1,4-bis(butyltelluro)-1,3-butadienes and a new route to transform them into tellurophene, 2-substituted or 2,5-disubstituted tellurophenes by means Te/Li exchange reaction followed by capture of intermediates.

RESULTS AND DISCUSSION

Synthesis of Tellurobutadienes. Limited reports on the synthesis of highly functionalized tellurobutadienes have appeared in literature.[11-13] We performed here the stereospecific hydrotelluration of conjugated 1,3-enynes **1-5** using ditelluride and sodium borohydride in ethanol

under nitrogen and reflux to produce the corresponding 1-organyltelluro-1,3-butadienes[12a,13b] with the generated double bond of *Z* configuration (Equation 1; Table 1). Stereochemical assignments of the double bonds bearing the tellurium moiety were made on the basis of chemical shifts and coupling constants since the *J*-values of a wide range of (*E*)- and (*Z*)-vinylic tellurides are known.[12b] We also observed that enynes with disubstituted triple bonds such as **6** and **7** fails completely to react in this way and only the enyne containing the propargylic triple bond **4** undergoes the butyltellurolate addition in good yield (entry 4; Table 1) since the hydroxyl group activate the triple bond toward the hydrotelluration.[14b] The following new butyltellurobutadienes employed in our studies were synthesized by employing this procedure: (1*Z*,3*Z*)-1-butyltelluro-4-methoxy-1,3-butadiene **8**, (1*Z*,3*Z*)-1-butyltelluro-3-methyl-1,3-pentadien-5-ol **9**, (1*Z*,3*Z*)-1,4-bis(butyltelluro)-1,3-butadiene **10**, (2*Z*,4*Z*)-2,5-bis(butyltelluro)-2,4-hexadien-1,6-diol **11** and the (1*Z*)-1-butyltelluro-2-hexenyl ethene **12**. Synthesis of **8** that is a very stable compound, is performed using an excess of enyne. Triple bond of compound **1** is deactivated probably by the presence of oxygen atom at C-1 as indicated by reaction time. In contrast, preparation of **10** from **3** that contains a tellurium atom bonded at C-1 (entry 3; Table 1) occurs in a shorter reaction time.



(1)

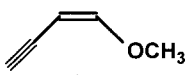
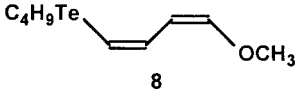
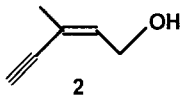
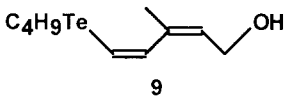
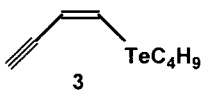
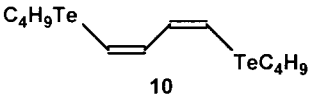
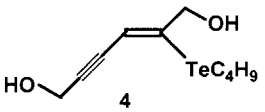
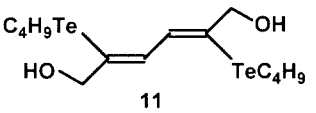
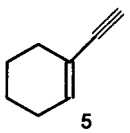
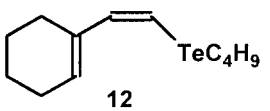
6, R = C_6H_5 R' = R"= H
7, R = C_5H_{11} R' = R"= H

The enynes precursors of **8** and **9** are commercially available, but for the synthesis of **10** and **11** was necessary the preparation of (*Z*)-butyltelluro butenynes **3** and **4**. We obtained compounds **3** and **4** by a controlled hydrotelluration of the corresponding 1,3-butadiynes.[14] However the preparation of **10** and **11** can be performed in a one pot procedure from the 1,3-butadiynes free of tellurium.

Dodecyl and p-methoxyphenyltelluro derivatives analogous to **9** and **12** were previously described[12] using the same method. In the present study we opted by the use of butyltelluro derivatives, since in reaction with butyllithium a symmetrical telluride is formed, that is easily

separated, but specially because the vinyl-tellurium bond cleavage is totally favored over butyl-tellurium bond cleavage. In reactions of aryl vinyl tellurides with butyllithium, Te-aryl and Te-vinyl bonds are cleaved depending on reaction time and a complex mixture of products can be obtained.[15c]

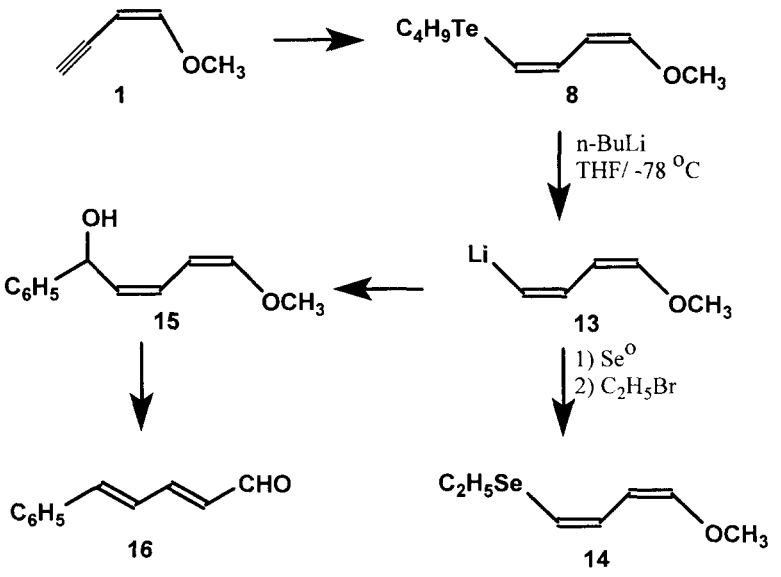
Table 1. Preparation of (*Z*,*Z*)-butyltelluro-1,3-butadienes by hydrotelluration of (*Z*)-1,3-enynes.

Entry	Reagent	Tellurobutadiene	Reaction time	Yield (%)
1	 **1**	 **8**	28 h	50
2	 **2**	 **9**	2 h	69
3	 **3**	 **10**	2 h	70
4	 **4**	 **11**	30 min	83
5	 **5**	 **12**	12 h	89

Te/Li exchange reaction on (1*Z*,3*Z*)-1-Butyltelluro-1,3-butadienes. The reaction of (1*Z*,3*Z*)-1-butyltelluro-4-methoxy-1,3-butadiene **8** with butyllithium in THF at -78 °C affords the (1*Z*,3*Z*)-butadienyllithium **13**, which reacts with elemental selenium followed by alkylation with ethyl bromide to give the (1*Z*,3*Z*)-1-ethylseleno-4-methoxy-1,3-butadiene **14** in 54% yield. Treatment of **13** with benzaldehyde affords the corresponding alcohol **15** in 53 % yield (Scheme 1). However, compound **15** is spontaneously and quantitatively transformed after some time (~ 48 h) into the 5-phenyl pentadienal **16** as confirmed by the analytical methods employed (^{1}H NMR, ^{13}C NMR, CG/MS, IR and elemental analysis). This transformation is also performed in 85 % yield by reaction of **15** with H_2SO_4 (50% aqueous sol.), SiO_2 and dichloromethane as solvent. It is noteworthy that pentadienals are important building-blocks in the synthesis of a range of polyunsaturated natural products,[8,17-21] such as trienes,[17] dienoates,[18] trienols[8a,18] of *Z*,*E* configurations and dienoates,[8a]

trienes[8a,20a] or tetraenes[20b] of ***E,E*** configurations. The synthesis of retinoids and retinal in both 13***Z*** and 13***E*** forms was also described recently using as intermediates enals obtained by organometallic additions to pyrylium salts.[21] In this way, we believe that the reaction developed here could be of great interest in organic synthesis and an alternative to preparation of dienals.

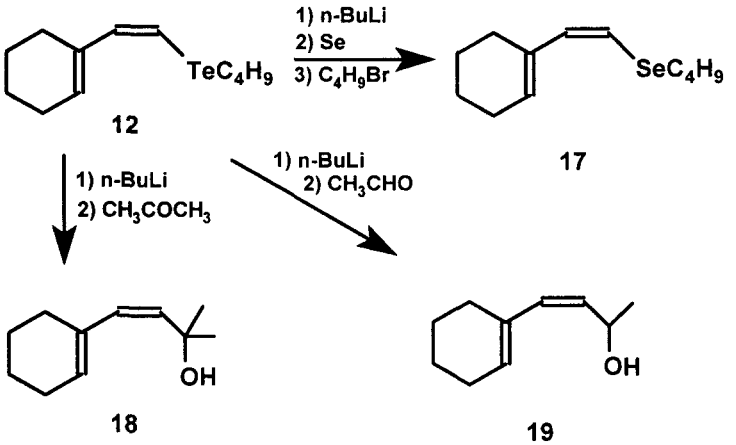
Scheme 1



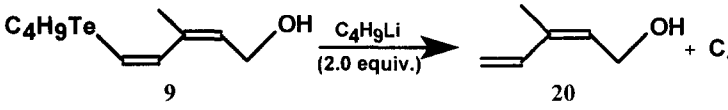
The ^{1}H NMR spectrum of **8** shows the coupling constants $J_{1,2}$ = 10.5 Hz and $J_{2,3}$ = 10.4 Hz of the olefinic protons of tellurium bearing double bond that resonates at 6,91 ppm (2-H) and 6,45 ppm (1-H), while olefinic protons of oxygen bearing double bond resonates at 5,92 ppm (4-H) and 4,96 ppm (3-H) with the coupling constants $J_{3,2}$ = 10.4 Hz, and $J_{3,4}$ = 6.6 Hz. These data clearly indicate the ***Z,Z*** configuration of compound **8**. No other isomers were detected by either GC/MS or ^{13}C NMR that presented only four olefinic signals (101.1; 108.1; 131.6 and 148.8). The conversion of **8** to **14** occurs with retention of configuration as indicate in the ^{1}H NMR spectrum by coupling constants $J_{1,2}$ = 9.3 Hz and $J_{2,3}$ = 10.6 Hz of olefinic protons of double bond bearing the selenium moiety that appears (resonate) up field 6.56 ppm (2-H) and 6.01 ppm (1-H) from that of the precursor **8**. Olefinic protons of double bond bearing the methoxy group in compound **14** resonates at 5.90 ppm (4-H) and 5.12 ppm (3-H) with $J_{3,2}$ = 10.6 Hz and $J_{3,4}$ = 6.6 Hz. In the ^{13}C NMR spectrum the four olefinic signals (104.3, 118.2, 124.4, 148.0) clearly indicate the isomeric purity of compound **14** that

was confirmed by CG/MS. The same stereocontrol was observed in transformations **12→17**, **12→18** and **12→19** (see experimental section).

Scheme 2



The Te/Li exchange reaction on compound **9** was accomplished with 2.0 equivalents of butyllithium in THF at -78 °C affording the (2*Z*)-3-methyl-2,4-pentadien-1-ol **20** in 57 % yield (Eq. 2). However, it was not possible to capture the butadienyllithium intermediate. We believe that the Te/Li exchange reaction must occur extremely fast and protonation of the Csp^2-Li bond probably occurs by the hydroxyl group before it can react with an added electrophile, but further studies are necessary to confirm this hypothesis.



(2)

The stereochemically pure dienyl selenide **17** was obtained on reaction of **12** with BuLi (1.1 equiv., THF, -78°C → r. t.) followed by insertion of selenium at room temperature and alkylation with butyl bromide. In the same way, compounds **18** and **19** were obtained from **12** with total retention of configuration after treatment of the butadienyllithium intermediate with acetone or acetaldehyde respectively. Fryzuk et al[6c] described the preparation of phenylseleno derivatives of ***E*** configuration at the selenium bearing double bond by the Zr/Se exchange reaction, analogous to the

alkylselenobutadienes **14** and **17** these authors studied the photochemical and termal induced isomerization of such compounds.

Although we not study the photochemical or thermal stability of **14** and **17**, it should be noted that the alkylselenobutadienes obtained by us were isomerically pure as determined by ^{1}H NMR. However **14** and **17** are stereoisomerically minus stable than tellurobutadienes analogues and undergo isomerization after some time.

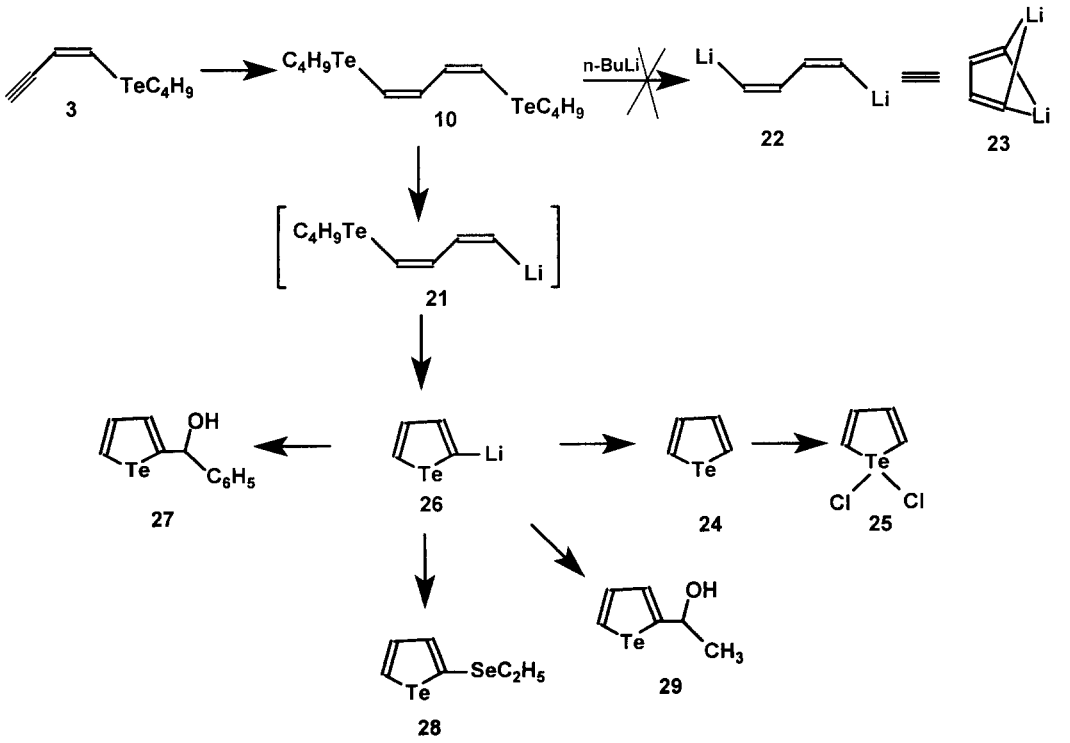
The formation and reactions of butadienyllithium reagents studied here, are stereospecific and always occur with retention of configuration,[22] while in the case of formation and reaction of (***Z,Z***)-1,4-diphenyl-1,4-dilithium butadiene from (***E,E***)-1,4-dibromo-1,4-diphenyl-1,3-butadiene a small amount of isomerization was observed.[23] It is important to emphasize that butadienyllithium obtained from a derivative of 2-bromo-1,3-butadiene and sec-butyllithium is configurationally unstable at temperature above -78°C furnishing 50% each of ***Z*** and ***E*** dienyl lithium.[6g]

Tellurophenes from Te/Li exchange reaction on 1,4-bis(butyltelluro)-1,3-butadienes. Tellurophenes were scarcely used to date in synthetic methodologies[16,24] probably because only a limitated number of methods for their preparation are known.[25] Recently we described our results on the synthesis, reactivity and mechanistics aspects of the chemistry of 3-iodotellurophenes and 3-butyltelluro-2,5-diphenyltellurophene.[14c] In this work we have discovered that treatment of 1,4-bis(butyltelluro)-1,3-butadiene **10** with 1.0 equivalent of butyllithium in tetrahydrofuran at -78°C affords the tellurophene **24** and dibutyl telluride as by product (Scheme 3). Formation of **24** was detected by ^{1}H NMR of the crude product and isolated by distillation on a Kugelrhor apparatus, however, to facilitate the manipulation and separation from dibutylteluride, compound **24** was transformed into the dihalogenated tellurophene **25** by treatment with sulfuryl chloride. The expected 1-butyltelluro-1,3-butadienyl-4-lithium **21** intermediate can not be trapped, since the ring closure occurs very rapidly. It is known that vinyl-tellurium bond cleavage is highly favored over alkyl-tellurium bond cleavage in alkyl vinyl tellurides[12-14] and the first Te/Li exchange in compound **10** to give **21** confirms this tendency, but the second cleavage is contrary since occurs the Te-butyl cleavage promoted intramolecularly by the butadienyllithium intermediate **21** at the ring closure step (Scheme 3). The more important feature to explain this fact is the large size and high polarizability of tellurium atom (soft atom) that is attacked by the vinyl anion to give the product that is stabilized by the ring aromaticity.[25a] On the other hand, when at position 4 of the butadienyllithium intermediate, an oxygen atom is bonded as in **13**, this reaction does not occur because the oxygen atom is not

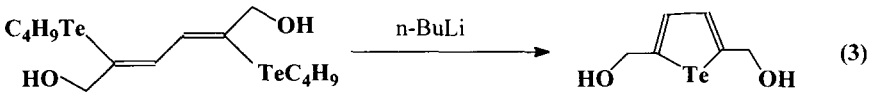
susceptible of attack by the vinyllithium anion since have a small size, low polarizability (hard atom) and no electrophilic character. In this way, the corresponding monolithium compound **13** can be trapped with different electrophiles (Scheme 1).

In attempt to obtain dilithio compound **22** from (1*Z*,3*Z*)-1,4-bis(butyltelluro)-1,3-butadiene **10** by Te/Li exchange reaction at C-1 and C-4 at same time, the reaction was accomplished by the fast addition of butyllithium to a solution in THF at -78°C and also by the inverse addition of **10** to butyllithium. However the dilithio intermediate **22** was not obtained. In these cases the formation of the heterocycle **24** is observed again and the deprotonation at α position occurs with the formation of α-lithiated tellurophene **26**, since the addition of benzaldehyde to the reaction mixture affords the 2-substituted tellurophene **27** (60 % isolated yield). Further evidence on the formation of this intermediate was obtained by insertion of elemental selenium into the C-Li bond and further alkylation with ethyl bromide. The 2-(ethylseleno)tellurophene **28** was isolated in 43 % yield (Scheme 3) from a mixture containing dibutyl telluride and the bad smelling butyl ethyl selenide by flash chromatography with hexane as eluent.

Scheme 3



The other bis(butyltelluro)-1,3-butadiene **11** obtained in this work was also submitted to reaction with n-BuLi in THF at -78 °C and the corresponding 2,5-disubstituted tellurophene **30** was obtained in 63% yield (Eq. 3). Compound **30** was purified by flash chromatography using a mixture of hexane/ethyl acetate (7/3) as eluent and identified by comparison with an authentic sample obtained as previously described.[26]



11 **30** (3)

It is known that derivatives of (1*Z*,3*Z*)-1,4-dilithio-1,3-butadiene **22** adopt a symmetrical bridge structure **23**[27] that are stabilized by a "Möbius-Hückel aromaticity"[28] or by favorable electrostatic interactions between carbon and lithium atoms in the bridge.[29] In this way we expected the formation of (1*Z*,3*Z*)-1,4-dilithio-1,3-butadiene now adding a complex butyllithium-TMEDA in ether at room temperature to a solution of (1*Z*,3*Z*)-1,4-bis(butyltelluro)-1,3-butadiene **10** in ether and further reaction with acetaldehyde to trap the dilithio compound **22**, but the dibutyl telluride and the substituted tellurophene **29** (50% yield) were obtained again. The relative ease of formation of tellurophenes would be a measure of differences in their stability compared to the dilithio compounds **22** derived from 1,4-dibutyltelluro-1,3-butadienes.

CONCLUSION

In conclusion, this work describes the synthesis and reactivity of several new monotellurobutadienes, ditellurobutadienes and a novel methodology to obtain substituted tellurophenes at the 2- and 2,5- positions. Studies on the scope and limitations of the transformation of (1*Z*,3*Z*)-1-butyltelluro-4-methoxy-1,3-butadiene **8** into 5-organyl pentadienals and their applications on the synthesis of natural products are underway in our laboratory and results will be published in due course.

EXPERIMENTAL SECTION

General remarks. ^{1}H and ^{13}C NMR spectra were recorded on a 80 MHz or a 300 MHz spectrometer as noted. GC/MS (using a HP-1 fused silica capillary column) and direct insertion spectra (EI) were measured at 70eV. Elemental analyses were performed at the Instrumental Analysis Center of the Chemistry Institute of São Paulo University. Reaction flasks and syringes were oven-dried (120°C) before use. Melting points (uncorrected) were determined on a Kofler hot plate. All reactions were carried out under an atmosphere of dry nitrogen and monitored by TLC using prepared plates (silica gel 60 F254 on aluminum). Merck silica gel (230-400 mesh) was used for flash chromatography. Ethanol (95%) from Merck was used and THF was distilled over sodium/benzophenone immediately before use. Dibutyl ditelluride was prepared by the method reported in the literature.[30]

(*Z*)-1-Butyltelluro-1-buten-3-yne (3). To a solution of 1,4-dichlorobutyne (6.0 g, 4.77 mL, 50 mmol) and pyridine (0.5 mL) in ethanol (15 mL), a solution of 40% NaOH (20 mL) was added dropwise during 30 min. maintaining the temperature between 70 to 75 °C under nitrogen. The butadiyne formed was captured through a canula in ethanol (10 mL) contained in another flask at -78 °C. To this solution, dibutyl ditelluride (2.96g, 8.0 mmol) and ethanol (20 mL) were added, followed by addition of $NaBH_4$ (0.9 g, 24 mmol). After the end of addition of $NaBH_4$, the dark red color disappearance was observed and the pale yellow solution was stirred at room temperature for 15 min. The product was diluted with ethyl acetate (70 mL) and washed with water (3 x 50 mL). After drying the organic phase over anhydrous $MgSO_4$, the solvent was removed under reduced pressure. The product **3** was obtained as a yellow liquid, pure for further use. Analytical sample was obtained by column chromatography using hexane as eluent. Yield: 1.77g (93%). MS m/z 238 (72.82) $C_8H_{12}Te$, 182 (100.00), 130 (87.39), 51 (94.46). ^{1}H NMR (80 MHz) (δ in $CDCl_3$) 0.90 (t, J = 6 Hz, 3H), 1.2-1.9(m, 4 Hz), 2.73(t, J = 6 Hz, 2H), 3.28(d, J = 2 Hz, 1H), 6.34(dd, J = 10.6 Hz, J $\cong$ 2 Hz, 1H), 7.37(d, J = 10.6 Hz, 1H). ^{13}C NMR 6.2, 13.1, 24.6, 34.0, 83.1, 83.8, 116.2, 122.2. *Anal* calcd. for $C_8H_{12}Te$: C, 40.75. H, 5.13. Found: C, 41.07. H, 5.18.

(*Z*)-2-Butyltelluro-2-hexen-4-yn-1,6-diol (4). To a solution of hexa-2,4-diyn-1,6-diol (0.22g, 2.0 mmol), dibutylditelluride (0.369g, 1.0 mmol), in 95% ethanol (40 mL) under N_2, $NaBH_4$ (0.11g, 3.0 mmol) was added at room temperature. After the red color disappearence, the yellow mixture was

heated at reflux for 15 min., allowed to reach room temperature, diluted with ethyl acetate (80 mL) and washed with brine (3 x 40 mL). After drying the organic phase over anhydrous $MgSO_4$, the solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel using a mixture of hexane/ethyl acetate (7/3) as eluent, to give the compound **4** as a yellow oil. Yield: 0.419 g (71%). MS m/z 298 (26.67), 129 (35.01), 94 (100.00), 57 (74.80). ^{1}H NMR (80 MHz) (δ in $CDCl_3$) 0.91(t, J = 7 Hz, 3H), 1.38 (sext., J = 7 Hz, 2H), 1.78 (quint., J = 7 Hz, 2H), 2.90 (t, J = 7 Hz, 2H), 3.31(broad s, 2H), 4.30(d, J ≅ 2.5 Hz, 2H), 4.43(d, J = 2.5 Hz, 2H), 6.39(t, J = 2.5 Hz, 1H). ^{13}C NMR 5.2, 13.1, 24.7, 33.6, 50.9, 60.3, 84.6, 93.9, 114.0, 134.2. *Anal.* calcd. for $C_{10}H_{16}TeO_2$: C, 40.59. H, 5.41. Found: C, 40.77. H, 5.48.

(1*Z*,3*Z*)-1-Butyltelluro-4-methoxy-1,3-butadiene (8). To a solution of 1-methoxy-but-1-en-3-yne **1** (sol 50% water:methanol (1:4), 0.2 g, 1.0 mL, 8.0 mmol) and dibutyl ditelluride (0.738g, 2.0 mmol) in ethanol (80 mL) at room temperature under nitrogen was added sodium borohydride (0.22 g, 6.0 mmol). After the end of addition, the yellow mixture was heated at reflux for 28 hours. Then it was cooled to room temperature, diluted with ethyl acetate (60 mL) and washed with NH_4Cl saturated solution (3 x 25 mL). After drying the organic phase over anhydrous $MgSO_4$, the solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel with hexane:ethyl acetate (9:1) as the mobile phase. After evaporation of hexane, the compound **8** that is very stable, was obtained as a yellow-orange oil. Yield: 0.541 g (50 %). MS m/z 270 (56.05) $C_9H_{16}OTe$, 213 (40.18) (-C_4H_9), 84 (100.00) (-C_4H_9Te); ^{1}H NMR (80 MHz) (δ in $CDCl_3$) 0.91(t, J = 7 Hz, 3H); 1.48(sext, J = 7 Hz, 2H); 1.78(quint, J = 7 Hz, 2H); 2.64(t, J = 7 Hz, 2H); 3.64(s, 3H); 4.96(ddd, J = 10.4 Hz, J = 6.6 Hz, J ~ 0.7 Hz, 1H); 5.92(dq, J = 6.6 Hz, J ~ 1.0 Hz, J ~ 0.7 Hz, 1H); 6.45(ddd, J = 10.5 Hz, J ~ 1.0 Hz, J ~ 0.7 Hz, 1H); 6.91(dd, J = 10.5, J = 10.4, 1H); ^{13}C NMR 6.4, 13.4, 24.9, 34.1, 60.1, 101.1, 108.1, 131.6, 148.8. *Anal.* Calcd. for $C_9H_{16}OTe$: C, 40.36. H, 6.02. Found: C, 40.73. H, 5.99.

(1*Z*,3*Z*)-1-Butyltelluro-3-methyl-1,3-pentadien-5-ol (9). This procedure was the same as that for **8**, except that 0.41 mL (0.384 g, 4.0 mmol) of freshly distilled (2*Z*)-3-methyl-pent-2-en-4-yne-1-ol **2** and dibutyl ditelluride (0.738g; 2.0 mmol) were used and the mixture was heated at reflux for 2 hours. Flash chromatography on silica gel with hexane:ethyl acetate (7:3) as eluent gave **9** as a yellow oil. Yield: 0.7g (69% yield). ^{1}H NMR (80 MHz) (δ in $CDCl_3$) 0.90(t, J = 7 Hz, 3H); 1.38(sext, J = 7 Hz, 2H); 1.80(quint, J = 7 Hz, 2H); 1.86(d, J ~ 0.5 Hz, 3H); 2.3(br s, 1H); 2.68(t, J =

7 Hz, 2H); 4.10(d, J = 7 Hz, 2H); 5.56(t, J = 7 Hz, 1H); 6.75(d, J = 10.6 Hz, 1H); 6.97(d, J = 10.6 Hz, 1H); ^{13}C NMR 7.2, 13.0, 21.4, 24.7, 33.7, 59.2, 105.8, 128.0, 135.5, 136.9. *Anal* Calcd. for $C_{10}H_{18}OTe$: C, 42.61. H, 6.44. Found: C, 42.95. H, 6.36.

(1*Z*,3*Z*)-1,4-bis(butyltelluro)-1,3-butadiene (10). The same procedure as for **8**, using the 1-butyltelluro-but-1-en-3-yne **3** (4.09g, 17,36 mmol), dibutyl ditelluride (3.20g, 8.68 mmol) and sodium borohydride (0.99, 26.04 mmol) in ethanol (80 mL), after 2 hours of reflux usual work-up and purification by column chromatography on silica gel using hexane as eluent, affords **10** as a yellow-orange liquid. Yield: 5.13g (70%). MS m/z 426 (0.00), 369 (3.67) ($C_4H_9TeC_4H_4Te$), 312 (3.57) ($C_4H_4Te_2^+$), 239 (42.58) ($C_4H_9TeC_4H_4^+$), 183 (53.02) ($C_4H_8Te^+$), 109 (22.16) ($C_8H_{12}^+$) 57 (100.00) ($C_4H_8^+$); ^1H NMR (80 MHz) (δ in $CDCl_3$) 0.93(t, J = 7 Hz, 6H), 1.42(sext, J = 7 Hz, 4H), 1.80(quint, J= 7 Hz, 4H), 2.70(t, J = 7 Hz, 4H), 6.5-7.1(m, 4H). ^{13}C NMR 6.8, 13.4, 24.8, 33.9, 108.6, 138.4. *Anal* Calcd. for $C_{12}H_{22}Te_2$: C, 34.19; H, 5.26. Found: C, 34.28: H, 5.28

(2*Z*,4*Z*)-1,4-bis(butyltelluro)-2,4-hexadien-1,6-diol (11). The same procedure as for **8**, using the (*Z*)-2-butyltelluro-hexa-2-en-4-yn-1,6-diol **4** (0.591g, 2.0 mmol), dibutyl ditelluride (0.367g, 1.0 mmol) and sodium borohydride (0.19g, 5.0 mmol) in ethanol (80 mL), after 30 minutes of reflux, usual work-up and purification by flash chromatography using hexane to elute the unchanged dibutyl ditelluride and ethyl acetate to elute the product **11** which was obtained as a yellow liquid after solvent evaporation under reduced pressure. Yield: 0.802 g (83 % yield). ^1H NMR (80 MHz) (δ in $CDCl_3$) 0.88(t, J = 7 Hz, 6H), 1.4(sext, J = 7 Hz, 4H), 1.76(quint, J = 7 Hz, 4H), 2.76(t, J = 7 Hz, 4H), 2.90 (broad s, 2H), 4.32(s, 4H), 6.90(s, 2H). ^{13}C NMR 6.5, 13.1, 24.6, 33.7, 70.2, 125.9, 137.4. *Anal* calcd. for $C_{14}H_{26}O_2Te_2$: C, 34.92. H, 5.44. Found: C, 35.13. H, 5.43.

(*Z*)-1-Butyltelluro-2-cyclohexenyl etene (12). The same procedure as for **8**, using the ethynyl cyclohexene **5** (0.637g, 0.70 mL, 6.0 mmol), dibutyl ditelluride (1.107g, 3.0 mmol) and sodium borohydride (0.33g, 9.0 mmol) in ethanol (80 mL), after 12 hours of reflux, usual work-up and purification by column chromatography using hexane as eluent give the compound **12** as a yellow oil. Yield: 1.5 g (89%). MS m/z 294 (15.25), 237 (44.94), 107 (100.00), 79 (57.62). ^1H NMR (80 MHz) (δ in $CDCl_3$) 0.92 (t, J = 6 Hz, 3H), 1.2-1.9 (m, 8H), 1.9-2.3 (m, 4H), 2.61 (t, J = 6 Hz, 2H), 5.5-5.7 (m, 1H), 6.46 (d, J = 8 Hz, 1H), 6.76 (d, J = 8 Hz, 1H). ^{13}C NMR 8.1, 13.1, 21.6, 22.3, 24.7,

25.2, 27.3, 33.6, 99.7, 127.7, 137.1, 139.1. *Anal* calcd. for $C_{12}H_{20}Te$: C, 49.38. H, 6.91. Found: C, 49.56, H, 6.91.

Te/Li exchange reaction on (1*Z*,3*Z*)-1-Butyltelluro-4-methoxy-1,3-butadiene (8). To a solution of **8** (0.267g; 1.0 mmol) in THF (8.0 mL), cooled to -78°C under N_2, BuLi (0.76 mL, 1.1 mmol, 1.43M) was added in one portion. The reaction mixture was stirred at this temperature and after 10 min, the butadienyl lithium **13** formed can be used *in situ*. The facts observed in reactions of these intermediate (total disappearence of **8** -followed by TLC- and formation of only one product) indicated that it is formed in high yield.

(1*Z*,3*Z*)-1-ethylseleno-4-methoxy-1,3-butadiene (14). To a solution of butadienyl lithium **13** formed as above, elemental selenium (0.079 g, 1.0 matg) was added, the cooling bath removed and the mixture stirred at room temperature until all selenium dissapeared (about 20 min), then ethyl bromide (0.08 ml, 1.1mmol) was added, the solution turned yellow and after 10 minutes of stirring was treated with a saturated solution of NH_4Cl, diluted with ether (30 mL) and washed with NH_4Cl saturated solution (3 x 15 mL). After drying the organic phase over anhydrous $MgSO_4$, the solvent was removed under reduced pressure and the residue purified by flash chromatography using hexane as eluent and the product **14** was obatined as a yellow oil. Yield: 0.104g (54 %). MS m/z 192(68.74) $C_7H_{12}OSe$, 163(100.00) ($-C_2H_5$). ^1H NMR (80 MHz) (δ in $CDCl_3$) 1.45(t, J = 7 Hz, 3H), 2.64 ((q, J = 7 Hz, 2H), 3.62(s, 3H), 5.12(dq, J = 10.6 Hz, J = 6.6 Hz, J ~0.7 Hz, 1H), 5.90(dt, J = 6.6 Hz, J ~0.7 Hz, 1H), 6.01 (dt, J = 9.3 Hz, J ~0.7 Hz, 1H), 6.56 (dq, J = 10.2 Hz, J = 9.3 Hz, J ~0.7 Hz, 1H). ^{13}C NMR 15.9, 19.9, 59.8, 104.3, 118.2, 124.4, 148.0.

(1*Z*,3*Z*)-1-methoxy-5-hydroxy-5-phenyl-1,3-pentadiene (15). To a solution of butadienyl lithium **15** formed as above, benzaldehyde (0.101 mL, 1.0 mmol) freshly distilled was added at -78°C and stirred for 30 minutes at this temperature, then allowed to reach room temperature and stirred for additional half hour. Work-up as for **14** affords compound **15** as a pale yellow liquid. Yield: 0.10g (53% yield). Compound **15** can be further purified by flash chromatography using a mixture of ethyl acetate/hexane (8/2) as eluent, however, prolongated contact with SiO_2 must be avoided since promotes hydrolysis of **15** to form compound **16**. MS m/z 190 (0.00), 172 (69.96) ($-H_2O$), 158 (25.55) ($-CH_3O$), 130 (16.00), 115 (100.00). ^1H NMR (300 MHz) (δ in $CDCl_3$) 2.47 (br s, 1H), 3.48 (s, 3H), 5.2-5.5 (m, 3H), 5.85 (d, J = 6.9 Hz, 1H), 6.40 (t, J = 11.5 Hz, 1H), 7.1-7.4 (m, 5H).

(2*E*,4*E*)-5-Phenyl-2,4-pentadien-1-al (16). MS m/z 158 (52.87) ($C_{11}H_{10}O$), 129 (100.00), 115 (59.82). ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 6.25 (dd, J = 15.7 Hz, J = 7.85 Hz, 1H), 6.9-7.1 (m, 2H), 7.25 (m, 1H), 7.35 (m, 3H), 7.48 (m, 2H), 9.61 (d, J = 7.85 Hz, 1H). ^{13}C NMR 125.7, 127.1, 128.5, 129.2, 131.1, 135.1, 141.9, 151.5, 192.9. *Anal* calcd. for $C_{11}H_{10}O$: C, 83.52. H, 6.37. Found: C 83.13. H, 6.41.

(2Z)-3-Methyl-2,4-pentadien-1-ol (20) by reaction of (9) with butyllithium. To a solution of **9** (0.37g, 1.32 mmol) in THF (8.0 mL) at -78°C under nitrogen, BuLi (1.85 mL, 2.64 mmol, 1.43 M in hexanes) was added in one portion . After 10 minutes at this temperature, the reaction mixture was allowed to reach room temperature, treated with water (0.2 mL), diluted with ethyl acetate (50 mL) and washed with saturated solution of NH_4Cl (3 x 20 mL). The organic phase was dried over anhydrous $MgSO_4$, the solvent evaporated under reduced pressure and the residue purified by flash chromatography using hexane to elute the dibutyl telluride: 0.224g (75% yield) and ethyl acetate to elute the tellurium free butadiene **20**: 0.112g (87% yield). MS m/z 98 (24.4) $C_6H_{10}O$, 83 (100.00), 69 (83.06), 55 (60.00). ^{1}H NMR (80 MHz) (δ in $CDCl_3$) 1.82 (d, J ~1.0 Hz, 3H), 3.58 (br s, 1H), 4.15 (d, J = 6.6 Hz, 2H), 5.07 (dq, J = 10.66, J ~ 1.0 Hz, 1H), 5.21 (dq, J = 17 Hz, J ~0.7 Hz, 1H), 5.48 (t, J = 6.6 Hz, 1H), 6.68 (q, J = 17 Hz J = 10.66 Hz, 1H).

(*Z*)-1-Butylseleno-2-cyclohexenyl ethene (17). To a solution of the tellurobutadiene **12** (0.291, 1.0 mmol) in THF (6.0 mL), n-BuLi (0.76 mL, 1.1 mmol; 1.43M in hexanes) was added at -78 °C and the solution was stirred for 15 min, then allowed to reach room temperature and elemental selenium (0.079g, 1.0 mmol) was added. After total disappearance of selenium, bromobutane (0.137g, 0.10 mL, 1.0 mmol) was added and the resulting mixture stirred for 1 hour. After usual work-up the product **17** was purified by distillation in a kugelrohr apparatus (150 °C/0.5 mmHg). Yield: 0.17g (70%). MS m/z 244 (12.09) 187 (100.00) 145(52.22) 105 (29.66). ^{1}H NMR (80 MHz) (δ in $CDCl_3$) 0.90 (t, J = 7 Hz, 3H), 1.2-1.9 (m, 8H), 2.0-2.4 (m, 4H), 265 (t, J = 6.66 Hz, 2H), 5.6-5.8 (m, 1H) 6.08 (d, J = 10.66 Hz, 1H), 6.30 (d, J = 10.66 Hz, 1H).

(*Z*)-2-Methyl-4-cyclohexenyl-3-buten-2-ol (18). To a solution of tellurobutadiene **12** (0.582g, 2.0 mmol) in THF (10 mL) at -78 °C under nitrogen, n-BuLi (1.43 mL, 2.0 mmol, 1.39 M in hexanes) was added in one portion and the solution stirred for 15 min. Then, acetone (0.116g, 0.14 mL, 2.0

mmol) was added and the reaction mixture stirred for 15 min at -78 °C and an additional 15 min at room temperature. After usual work-up, the product **18** was purified by flash chromatoraphy using a mixture of hexane/ethyl acetate (8/2). Yield: 0.199g (60%). MS m/z 166 (35.53), 151 (72.67), 105 (93.32), 91 (100.00), 79 (72.10). ^{1}H NMR (80 MHz) (δ in $CDCl_3$) 1.30 (s, 6H), 1.5-1.7(m, 4H), 1.9-2.1(m, 4H), 3.0 (br s, 1H), 5.42(d, J = 13.3, 1H), 5.6-5.8 (m, 2H). ^{13}C NMR 21.7, 22.2, 25.0, 29.1, 31.3, 72.1, 125.1, 129.0, 137.2, 137.3. *Anal.* calcd for $C_{11}H_{18}O$: C, 84.61. H, 11.53. Found: C, 84.68. H, 11.73.

(*Z*)-4-Cyclohexenyl-3-buten-2-ol (19). To a solution of the tellurobutadiene **12** (0.291, 1.0 mmol) in THF (6.0 mL) at -78 °C under nitrogen, n-BuLi (0.76 mL, 1.1 mmol, 1.43 M in hexanes) was added in one portion and after 15 min under stirring, acetaldehyde (0.09 mL, 2.0 mmol) was added. The reaction mixture was maintained at -78 °C for 15 min and then 2 h at room temperature. After usual work-up the product **19** was purified by filtration on silica gel using a mixture of hexane/ethyl acetate (8/2). Yield: 0.098 (65%). MS m/z 152 (21.95), 87 (65.67), 79 (100.00), 67 (67.97). ^{1}H NMR (80 MHz) (δ in $CDCl_3$) 0.71-1.13(m, 4H), 1.25(d, J = 8 Hz, 3H), 1.49-1.85(m, 2H), 1.9-2.3(m, 2H), 4.78(dq, J = 8 Hz, J = 5.9 Hz, 1H), 5.20(dd, J = 12 Hz, J = 8 Hz, 1H), 5.63(m, 1H), 5.78(d, J = 12 Hz, 1H). *Anal.* calcd for $C_{19}H_{16}O$: C, 87.69. H, 6.15. Found: C, 87.78. H, 6.04.

Dichloro tellurophene (25) by reaction of (1*Z*,3*Z*)-1,4-bis(butyltelluro)-1,3-butadiene with butyllithium. To a solution of (1*Z*,3*Z*)-1,4-bis(butyltelluro)-1,3-butadiene **10** (0.842 g, 2.0 mmol) in dry THF (16 mL) at -78°C under nitrogen and stirring, BuLi(0.62 mL, 1.0 mmol, 1.43 M in hexanes) was added in one portion. After 15 minutes at this temperature, the mixture was allowed to reach room temperature, treated with water (0.5 mL), diluted with ether (40 mL) and washed with a saturated solution of NH_4Cl (3 x 25 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue is formed by dibutyl telluride and tellurophene **24** as confirmed by ^{1}H NMR spectroscopy, which can be separated by distillation (45 °C/20 mmHg). This mixture was diluted in petroleum ether and sulfuryl chloride (1.0 mL) was added dropwise (excess) and the yellow solution turned white with precipitation of a white solid. The solvent was partially evaporated and the precipitate filtered, washed with ethyl acetate and dried under vacuum to give the pure dichloro tellurophene **25** which was recrystallized by addition of petroleum ether to a solution of **25** in ethyl acetate. m.p. = 118-120 °C. Yield: 0.307g (61 %). ^{1}H NMR (80 MHz) (δ in C_3D_6O): 7.58(dd, J = 8 Hz, J = 2.6 Hz, 2H) 8.58(dd, J = 8 Hz, J = 2.6 Hz, 2H) ^{13}C NMR: 145.3 and

146.8. *Anal.* calcd for $C_4H_4TeCl_2$: C, 19.17. H, 1.61. Found: C. 19.42. H, 1.63. The solvent of the remain solution was evaporated under reduced pressure to give the pure dibutyltelluro dichloride. Yield: 0.456 g (73%). ^1H NMR (δ in $CDCl_3$): 1.06(t, J = 7 Hz, 6H), 1.58(sext, J = 7 Hz, 4H), 2.16(quint, J = 7 Hz, 4H), 3.48(t, J = 7 Hz, 4H).

2-(Ethylseleno)tellurophene (28). To a solution of **10** (0.842g, 2 mmol) in dry THF (16 mL) at -78°C under nitrogen with stirring, BuLi (1.52 mL, 2.2 mmol, 1.43 M in Hexane) was added at once the solution turned orange-red. After 5 minutes at this temperature, the mixture was allowed to reach room temperature, elemental selenium (0.158g, 2 mmol) was introduced and the mixture stirred until complete disappearance of selenium (~20 minutes), then ethyl bromide (0.6 mL, excess) was added and the stirring was continued for an additional 20 minutes. Work-up as above furnished a residue containing dibutyltelluride, butyl ethylselenide and 2-ethylseleno tellurophene **28** which was obtained in a pure form by flash chromatography using hexane as eluent. Yield: 0.246g (43%). MS m/z 288 (42.28), 259 (13.81), 132 (75.81), 51 (100.00). ^1H NMR (80 MHz) (δ in $CDCl_3$) 1.48(t, J = 7,4 Hz, 3H), 2.83(q, J = 7.4 Hz, 2H), 7.51(dd, J = 6 Hz, J = 3.3 Hz, 1H), 7.7(dd, J = 3.3 Hz, J = 1.1 Hz, 1H), 8.87(dd, J = 6 Hz, J $\cong$ 1.1, 1H); ^{13}C NMR, 15.2, 26.7, 125.3, 130.6, 137.6, 143.7; *Anal* calcd for C_6H_8TeSe: C, 25.14. H, 2.81; Found: C, 25.44. H,2.80.

2-(Hydroxybenzyl)tellurophene (27). The same procedure as for **28**, but instead of selenium, benzaldehyde was added (0.203 mL, 2.0 mmol) at -78°C, the solution turned orange-red to yellow and the reaction was stirred for an additional 40 minutes at room temperature. Work-up as above furnished a residue containing dibutyl telluride, compound **27** and benzylic alcohol. This mixture was filtered on silica gel eluting with hexane to remove dibutyl telluride and with ethyl acetate to remove other polar substances that were further separated by horizontal distillation in a Kugelrohr apparatus under vacuum. The last fraction to distill (160 °C/0.5mmHg) is the white solid product **27**. Yield: 0.345g (60 % yield). MS m/z 288 (11.72), 157 (39.76, 128 (31.62), 105 (100.00). ^1H NMR (80 MHz) (δ in $CDCl_3$): 2.77(br s, 1H), 5.82(d, J $\cong$ 1.2 Hz,1H), 7.2-7.5(m, 6H), 7.67(dd, J = 6.6 Hz, J = 4.0 Hz, 1H), 8.80(dd, J = 6.6 Hz, J $\cong$ 1.1 Hz, 1H); ^{13}C NMR: 76.7, 126.0. 126.2, 127.9, 128.6, 133.6, 137.4, 144.4, 157.1; *Anal* calcd for $C_{11}H_{10}OTe$: C, 46.21. H, 3.50; Found: C, 46.53. H, 3.51.

2-(1-Hydroxyethyl)tellurophene (29). To a solution of TMEDA (0.64 mL, 4.3 mmol) in ethyl ether (15 mL) at room temperature under nitrogen and stirring, BuLi (1.4 mL, 2.0 mmol, 1.43M in

hexanes) was added in one portion, after 5 minutes this white mixture was transferred with a syringe to a round bottomed flask containing a solution of (1*Z*,3*Z*)-bis(butyltelluro)-1,3-butadiene **11** (0.421g, 1.0 mmol) in ethyl ether (5 mL). The resulting solution was stirred during 30 minutes and acetaldehyde (0.11 mL, 2 mmol) was added; at the end of addition the solution turned orange. The stirring was continued for an additional 20 minutes, the mixture was diluted with ethyl acetate (40 mL) and washed with saturated solution of NH_4Cl (3 x 20 mL). The organic phase dried over anhydrous $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was purified by flash chromatography using a mixture of hexane/ethyl acetate (8/2) as eluent to affords the product **29**. Yield: 0.111g (50 %). MS m/z 226 (15.71 C_6H_8OTe, 183 (21.34), 95 (61.32), 53 (100.00). ^1H NMR (80 MHz) (δ in $CDCl_3$): 1.40(d, J = 6.66 Hz, 3H), 3.32(br. s, 1H), 4.81(dq, J = 6.66 Hz, J = 1.0 Hz, 1H), 7.29(dt, J = 4.0 Hz, J ≅ 1.3, 1H), 7.58(dd, J = 6.6 Hz, J = 4.0 Hz, 1H), 8.62(dd, J = 6.6 Hz, J ≅ 1.3 Hz, 1H). ^{13}C NMR: 27.2, 70.5, 124.2, 131.1, 136.8, 160.1 *Anal* calcd. for C_6H_8OTe: C, 32.21, H, 3.60 Found: C, 32.52. H, 3.64.

2,5-bis(Hydroxymethyl)tellurophene (30). (2*Z*,4*Z*)-1,4-bis(butyltelluro)-2,4-hexadien-1,6-diol **11** (0.586g, 1.21mmol) in THF at -78°C under nitrogen was treated with BuLi (3.4 mL, 4.9 mmol, 1.43 M in hexanes) in one portion. The reaction mixture was stirred for 10 minutes, allowed to reach room temperature, water was added and after usual work-up a mixture of dibutyl telluride and 2,5-bis(hydroxymethyl) tellurophene **30** was obtained. They were separated by flash chromatography using a mixture of hexane/ethyl acetate (7/3) to give the compound **30** as a yellow solid. Yield: 0.174g (60 %) of **30**. mp 106-107 °C. MS m/z 242 (26.74), 130 (27.63), 94 (42.46), 66 (100.00). ^1H NMR (80 MHz) (δ in $CDCl_3$): 4.67(d, J = 4.8 Hz, 4H), 4.95 (t, J = 4.8 Hz, 2H), 7.28(s,2H)

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