Iodocyclization of (*Z*)-1-(Butyltelluro)-1,4-diorganylbut-1-en-3-ynes. Synthesis and Reactions of 3-Iodotellurophenes

Miguel J. Dabdoub,* Vânia B. Dabdoub, and Marco A. Pereira

Laboratório de Síntese de Compostos Organocalcogênios, Departamento de Química, FFCLRP, Universidade de São Paulo, Av. Bandeirantes, 3900-Ribeirão Preto, SP, Brazil

Julio Zukerman-Schpector

Departamento de Química, Universidade Federal de São Carlos, São Carlos, SP, Brazil

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The iodocyclization of (*Z*)-tellurobutenynes **5a**−**g** by reaction with I_2/petroleum ether was studied in detail. 3-Iodotellurophenes **7a**−**f** were formed, and optimum conditions to obtain these compounds in high yields were established. The reaction involves attack of iodide at the initially formed intermediate of type **10** followed by ring closure that is favored by the strong aromatic character of the resulting products. Two possible and alternative pathways for the ring closure are proposed to explain our observations: (a) transformation of **10** to **11** that undergoes further cyclization to give **7a**−**f** (pathway a) or (b) direct cyclization of **10** to give tellurophene diiodide **9** (pathway b). The products and side products obtained are in agreement with the proposed mechanisms. Formation of **7a** from ditelluride **14** and iodine provides additional evidence of the intermediacy of **11** (in pathway a). Structures of **7a** and **5g** were elucidated by X-ray crystallography. In the case of compound **5e**, where a terminal triple bond was present, the resulting intermediate of type **10** also underwent the attack of iodide directly at the terminal carbon to give compound **12** together with **7e**. Ring-opening of 3-iodotellurophene **7a** occurs by reaction with *n*-butyllithium to form acyclic ditelluride **14** or monotelluride **16** depending on the alkyllithium amounts employed. Plausible mechanisms for these novel reactions are proposed and supported. Conversion of **7a** to 3-(butyltelluro)-2,5-diphenyltellurophene (**22**) was carried out readily by an unusual "aromatic nucleophilic substitution" using the butyl tellurolate anion.

Introduction

The growing interest in enediyne structure in chemical, biological, and medical research is a result of the ubiquity of this structure in an important class of anticancer antibiotics derived from bacterial sources. The structures of neocarzinostatin chromophore,[1] calicheamicins,[2] esperamicins,[3] and dynemicin A[4] have been reported since 1985. More recently (1993), other enediyne antibiotics were discovered such as kedarcidin chromophore[5] and C-1027 chromophore.[6] The excitement surrounding these molecules lies in their molecular structure, their important biological activity, and their mode of action.[7] In 1991, Nicolau and Dai[7a] reviewed the chemistry and biology of the enediynes discussing the mechanistic, synthetic, molecular design, and DNA cleavage aspects associated with enediyne compounds. Many papers concerning several aspects of these structures have been published.[8] Methodologies for the synthesis of enyne or enediyne compounds are of great interest, especially with regard to synthesis of these enediyne cytostatic/antibiotics or similar molecular models.[8,9]

trans-Enynes or *cis*-enynes are also found in a wide range of natural products extracted from several natural sources. Brasilenyne, obtusenyne, *cis*-dihydrorhodophytin, and others were isolated from *Laurencia red algae*[10] or from a green variety of the Hawaiian algae *Laurencia nidifica*.[11] *cis*-Enynes are also obtained from seahares,[12]

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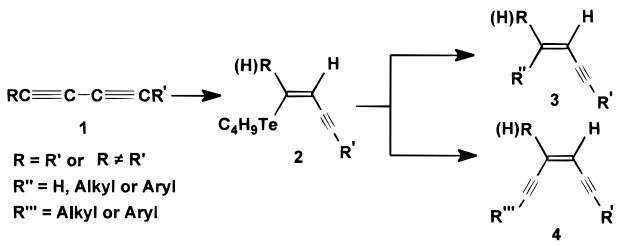
Scheme 1



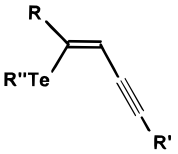
sponges,[13] or South American "poison arrow" frogs.[14] Chondriol[10] and *Laurencia thyrsifera*[15] are examples of known *trans*-enynes also isolated from *Laurencia red algae*. Thus, we had a special interest in the construction of enyne and enediyne systems with a defined configuration at the generated double bonds, using tellurium-containing intermediates.[16] To this end, the 1,3-butadiynes **1** were transformed into **2** by reaction with butyltellurolate anion generated from dibutyl ditelluride and $NaBH_4$ in ethanol (Scheme 1). The Te−H additions take place regio-[16] and chemoselectively.[16b] The stereochemistry of the new C−C double bond is defined *via* a *trans*-stereospecific process.[16b] Vinylic tellurium species[17] are important in organic synthesis since the tellurium moiety can be replaced by different organic groups always with total retention of configuration. Most of these reactions involve transmetalation to form the corresponding lithium,[16,18] copper,[18d,19] magnesium,[20] calcium,[20] sodium,[20] or zinc[19d,21] vinylic intermediates. The versatility of the tellurobutenyne approach could be greatly enhanced if tellurium-free enynes **3** or enediynes **4** with diverse chemical structures could be readily synthesized from it. These facts compelled us to study in detail the chemistry of tellurobutenynes of type **2**.

In this context, recent work by our group[16] as well as others[19] has shown that transmetalation/alkylation or transmetalation/cross coupling represents a new and useful method for the construction of a variety of stereodefined tellurium-free butenynes **3** and enediynes **4** (Scheme 1). We report in this paper that during our investigations of the chemistry and applications of 1-(butyltelluro)but-1-en-3-ynes[16] we discovered that these compounds undergo cleavage of the Te−Csp^3 bond in reaction with iodine, yielding a new class of tellurium compounds: the 3-iodotellurophenes. Ring opening of this class of molecules by reaction with *n*-BuLi permitted us to also prepare the previously unknown bis(enynyl) mono- and ditellurides. Studies defining the scope, limitations, and mechanistic aspects of these reactions have led us to a very good understanding of the overall process.

Results and Discussion

As discussed above, we have a special interest in the stereochemistry and regiochemistry of vinylic tellurium species. In recent papers,[16] we described the hydrotelluration of 1,4-diorganyl-1,3-butadiynes as a good methodology to obtain (*Z*)-1-(butyltelluro)-1,4-diorganylbut-1-en-3-ynes and the stereospecific lithium/tellurium exchange reaction in these compounds to give the tellurium-free (*E*)-1,4-diorganylbut-1-en-3-ynes, after aqueous workup[16a] or the corresponding (*Z*)-isomers after reaction of the terminal enynyl lithium intermediates with electrophiles.[16b]

In the case of tellurobutenynes **5d**−**f** the regio- and stereochemistry are easily determined by ^1H NMR. If R groups are aromatic, a more detailed analysis is necessary. All tellurobutenynes **5a**−**f** obtained are liquids. It



5a R=R'= C_6H_5 ; R''= C_4H_9 **5d** R=R'=CH_3; R''= C_4H_9
5b R=R'=p-$CH_3C_6H_4$; R''= C_4H_9 **5e** R=R'= H ; R''= C_4H_9
5c R=R'=p-$CH_3OC_6H_4$;R''= C_4H_9 **5f** R=H; R'= C_6H_5; R''= C_4H_9
5g R=R'=C_6H_5 ; R''= p-$CH_3OC_6H_4$

is known that diorganyl tellurides can be transformed into solid diiodo derivatives.[22] At the beginning of our studies we attempted to prepare the diiodo derivative **6** by treatment of the first tellurobutenyne obtained (**5a**) with iodine in petroleum ether at room temperature. By obtaining this solid derivative it would be possible to confirm the regio- and stereochemistry of **6** by X-ray diffractometry and consequently of **5a**.

When **5a** and iodine were combined at a 1:1 or 1:2 molar ratio, the expected adduct **6** was not isolated. After aqueous workup, this reaction results in a unique product containing tellurium. In the ^1H NMR spectrum of the obtained product the corresponding signals for the butyl group are not observed, but phenyl signals (10H) and a

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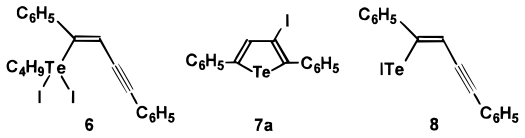
singlet at 7.9 ppm (1H) appear clearly. The mass spectrum and elemental analysis indicate the empirical formula $C_{16}H_{11}TeI$. Initially, the structures of isomers **7a** and **8** were proposed, and some facts were considered to choose from both structures. Firstly, the obtained



compound is exceptionally stable for an organyltellurenyl iodide, since simple aryltellurenyl halides are polymeric and thermally unstable.[23] However, 2-naphthyltellurenyl iodide is an exception to this rule.[23a] Other organyltellurenyl halides have been isolated when they have their stability enhanced by chelation with donor groups incorporated into the molecule.[24] In this way, carbonyl,[24a–c] nitro,[24d] and azo[24e] groups linked at the ortho position in aryltellurenyl halides strongly stabilize these compounds by formation of an intramolecular dipole. Similarly, benzyltellurenyl[25a] and propenoyltellurenyl[25b] halides are strongly stabilized by formation of an intramolecular dipole and have been isolated. Other analogous compounds such as the more frequently used phenyltellurenyl[26] or butyltellurenyl[17,18e,27] halides are obtained and used only *in situ*. Secondly, the infrared spectrum of the new compound obtained by us does not display a band corresponding to the triple bond (2000−2500 cm^{-1}). Another, and perhaps more important observation, is that in the ^1H NMR spectrum of **5a** the singlet corresponding to the vinylic proton appears at 6.34 ppm and after reaction with iodine the corresponding signal in the resulting compound undergoes a positive enhancement of 1.56 ppm resonating now at 7.9 ppm. We propose that the obtained compound must have a strong aromatic nature (or marked aromaticity). All observations were in accordance with the structure of 3-iodo-2,5-diphenyltellurophene **7a**. This conclusion was substantiated by a study of the crystal structure of the obtained product by X-ray diffraction.[28]

This result confirms the assignment made in our previous work[16a] for the regio- and stereochemistry of **5a**−**c**. The formation of 3-iodo-2,5-diorganyltellurophenes **7a**−**f** is only possible with tellurium bonded to carbon 1,

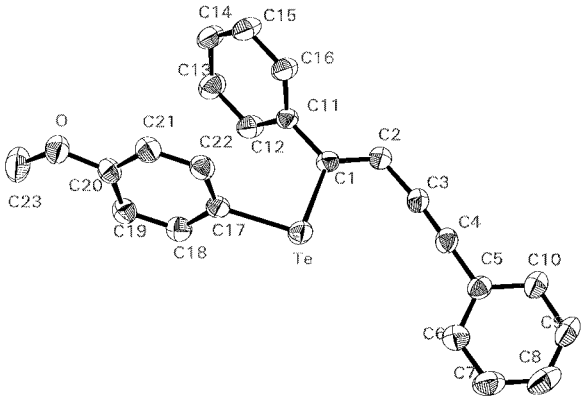
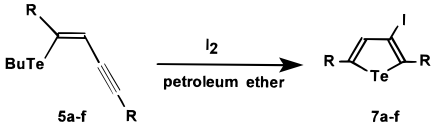


Figure 1. ORTEP drawing of **5g**. Atoms are represented by ellipsoids corresponding to 50% probability.

and the *Z* configuration of the double bond is necessary to permit ring closure. All results show that tellurolate



anions always attack carbon 1, of the butadiyne system by an anti-addition process.[16] These facts were additionally confirmed by X-ray analysis of crystals of **5g** that were grown from petroleum ether, the compound being a solid due to the presence of a *p*-methoxyphenyl group. We note that in the crystal structure of **5g** (Figure 1) the C17TeC1C2C3C4 moiety and the phenyl rings are coplanar. The Te−C=C angle of 118.4(3)° and C=C−C-(C_6H_5) of 123.2(4)° indicate the absence of important steric effects in this compound. This geometry probably is very similar for compounds **5a**−**f** and has also been suggested to contribute to the ring closure. However, the presence of the butyltellurium group is essential since iodocyclization with **5g** does not occur (see discussion below).

There are no reports in the literature on the synthesis of 3-iodotellurophenes. Because of the efficiency and reproducibility of the iodo-promoted cyclization of tellurobutenynes, this new reaction was studied in considerable detail. The iodo cyclization described herein proved to be efficient for the synthesis of 3-iodotellurophenes since reactions of substrates **5a**−**f** with iodine were successfully performed (Table 1). In all cases 2.0 equiv of iodine was necessary to bring the reaction to completion within the times indicated in Table 1. The crude reaction products were washed with an aqueous solution of sodium thiosulfate[30] to remove excess iodine. Formation of tarry and very low soluble products was also observed, thus leading to lower yields of **7**. The tarry products are the diiodotelluro-3-iodotellurophenes **9**, as confirmed by analysis of recrystallized product **9a** obtained from reaction of **5f** (Table 1, entry 8). The ratios of **7** and **9** were not determined for all runs. For reactions of **5a**−**d** the yields of **7** are reasonable, since formation of **9** is unfavorable due to the presence of substituents at positions 1 and 4. For **5f**, the minor steric hindrance permits the formation of **9a** as the major product (45% yield, Table 1, entry 8). However, when the organics were washed with aqueous sodium borohydride to remove

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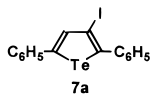
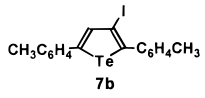
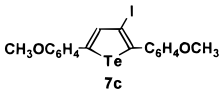
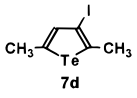
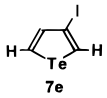
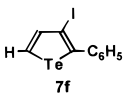
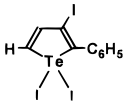
Table 1. 3-Iodotellurophenes Obtained

Entry	Product	m.p. (°C)	Yield(%)
1	 7a	105-106	83
2	 7b	122-124	82
3	 7c	130-131	80
4	 7d	*a*	90
5	 7e	37-37,5	40
6	 7f	*a*	80
7	 7g	*b*	4*c*
8	 9a	108-109	45*d*

a Liquid product purified by flash chromatography. *b* Liquid product purified by horizontal distillation (140 °C/0.1 mmHg). *c* Side product obtained by reaction of **1e** with 3 equiv of I_2 for 4 h. *d* Obtained when washed with sodium thiosulfate instead of $NaBH_4$.

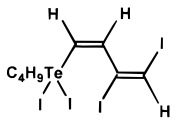
excess iodine,[31] yields of **7** were very good in most cases (entries 1−4 and 6; Table 1), since very efficient transformation of **9** to **7** was also promoted (Figure 2). After treatment with $NaBH_4$, the crude reaction products were routinely analyzed by ^1H NMR and CG/MS. In all cases, the formation of 3-iodotellurophenes was unequivocally determined by these techniques and no more tarry products were obtained.

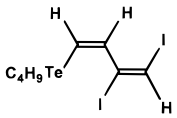
Iodobutane was detected as a side product in these reactions but not quantified. One possible explanation for the formation of the observed products is the mechanism proposed in Figure 2 that illustrates the tellurobutenyne **5a** reacting with 2 equiv of iodine to generate the (diiodotelluro)butadienyl iodonium intermediate **10** and iodide. Reaction with iodide transforms **10** into iodobutane and tellurenyl iodide **11**, which undergoes later attack of an iodide at the iodo atom, followed by ring closure through a "nucleophilic substitution" at the iodonium ion by the remaining electron pair of the tellurium atom to give the 3-iodotellurophenes **7a**−**f** (pathway a, Figure 2). Alternatively, **10** can undergo direct ring closure when attacked by iodide to give the tellurophene dihalogenated at the tellurium atom **9** and iodobutane (pathway b, Figure 2). However, compounds of type **9** can be formed by reaction of **7** with iodine present in the reaction medium (pathway a, Figure 2).

Reaction of (*Z*)-1-(butyltelluro)but-1-en-3-yne **5e** with 2.0 equiv of iodine after 1 h at room temperature afforded **7e** in only 40% yield (Table 1, entry 5) and **12** that is an insoluble tarry product. Tellurium was dehalogenated in compound **12** by reaction with $NaBH_4$ in a THF/H_2O mixture to give **13** that was identified by ^1H NMR. Attempts to perform further purification of **13** by distillation at 84 °C/0.01 mmHg results in loss of iodine affording **5e**. The presence of a butyl group in the structure of **12** and **13** indicates that cleavage of the Te−Csp^3 bond to form iodobutane occurs only if the ring closure is possible. Formation of **12** is explained by the direct attack of iodide at the terminal carbon atom in the iodonium intermediate of type **10**. In the other examples this side reaction was not observed, probably due to the steric hindrance caused by the presence of one substituent at the terminal carbon of iodonium ion (Table 1, entries 1−4 and 6).

When we performed the reaction of **5e** with 3.0 equiv of iodine and increased the reaction time to 4 h, the 2,3-diiodotellurophene **7g** was detected by CG/MS and ^1H NMR and separated from **7e** (Table 1, entry 7) by distillation in a Kugelrohr apparatus at 140 °C/0.1 mmHg in very low yield (4%). Ring closure for **5a**−**f** was always favored, but reaction of **5g** with I_2 (1:2 molar ratio) in petroleum ether failed completely. Ring formation is not possible in this case because nucleophilic attack of iodide against the *p*-methoxyphenyl group instead of the butyl group in the intermediate of type **10** (see Figure 2) is very unfavorable.

Stable diiodotelluro[22a] and dichlorotelluro[27a,32] monounsaturated compounds analogous to **6** and preparation *in situ* of monoalkenyl tellurenyl bromides[33] and iodides[27a] by reactions of divinyl ditellurides with halides are known. However, in reaction of **5a**−**f**, compounds of type **6** cannot be isolated or the intermediates of type **8** trapped *in situ* because the conjugated triple bond permits the ring closure that is highly favored by the aromaticity of the product formed. The formation of diiodotellurobutadiene **12** described here is equivalent to trapping an intermediate of type **10**.


12


13

Although the results obtained are quite consistent with **11** being an intermediate, the structure of the products **7a**−**f** would be accommodated by pathway b of the proposed mechanism. In order to support the hypothesis more forcefully it appeared desirable to find a reaction that would give reliable indication by its structural outcome that **11** had been an intermediate. In this way, interesting evidence for the mechanism proposed in Figure 2 was obtained by reacting compound **14** with iodine. Here the expected intermediate is the enynyltellurenyl iodide **8**[27a] that undergoes electrophilic addition of iodine at the triple bond to give the intermediate **11.** The last step of the mechanism involves an attack by iodide against **11** as depicted in Figure 3, leading directly to the exclusive formation of **7a** in 50% yield. The last reaction is an additional evidence that iodocyclization of **5a**−**f** can occur also by pathway a (Figures 2 and 3).

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

(32) Stefani, H. A.; Comasseto, J. V. *Organometallics* **1991**, *10*, 845.

(33) Dabdoub, M. J. Tese de Doutoramento, Inst. de Química, Univ. de São Paulo, 1989.

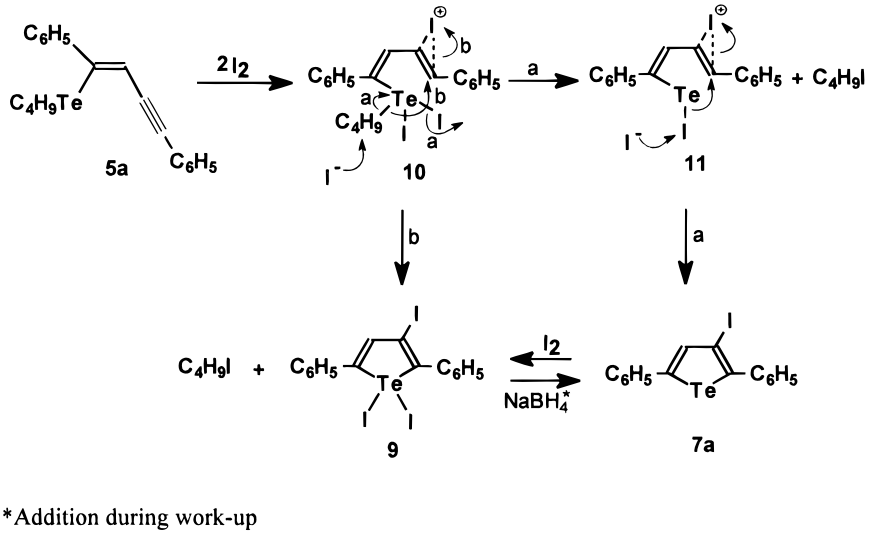


Figure 2. Proposed mechanism for the ring closure of 1-(butyltelluro)-1,4-diorganylbut-1-en-3-ynes.

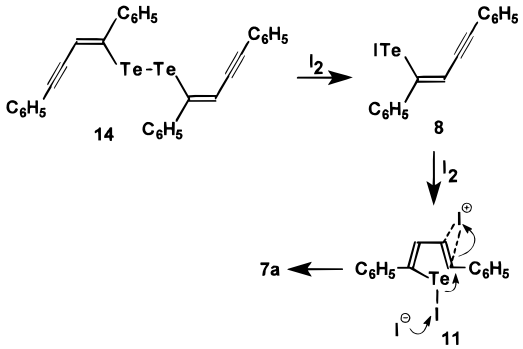
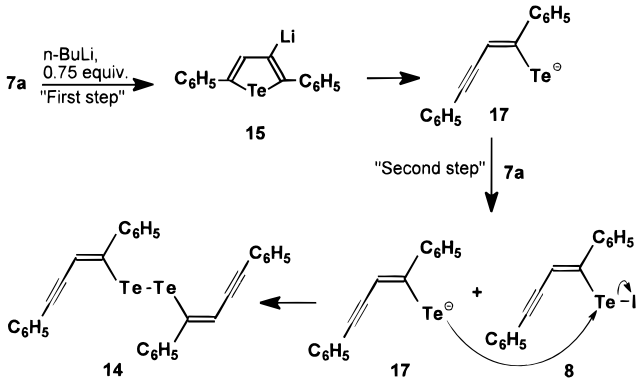


Figure 3.

Scheme 2



It is known that 3-bromo-[34] or 3-iodoselenophenes[35] that cannot be obtained by direct monohalogenation of unsubstituted selenophene[36] are obtained by reduction of 2,3,5-tribromoselenophene or 2,3,4,5-tetraiodoselenophene, respectively. Tellurium analogues are unknown, and reaction of unsubstituted tellurophene with bromine in methanol results in one product containing two bromine atoms bonded to the tellurium.[37] It is very difficult to introduce a substituent at the tellurophene β position if α positions are not occupied, since the latter positions are more reactive. Thus, few β-monosubstituted tellurophenes are known such as the 3-methyl[38] 3-phenyl[39] 4-methyl[38a] and 4-(hydroxymethyl)[40] derivatives.

In one experiment, the 2,5-diphenyl-3-iodotellurophene obtained in this work was metalated at the β-position by reaction with magnesium in THF. The Grignard intermediate obtained from **7a** was treated with water, furnishing the 2,5-diphenyltellurophene identified by comparison with an authentic sample obtained as previously described.[41] However, several attempts to reproduce this reaction were unsuccessful, and in most experiments starting material was recovered unchanged. In this way, (3-tellurophenyl)magnesium iodide cannot be used as a nucleophilic intermediate for the synthesis of different 3-substituted tellurophenes.

Our investigation was then extended to obtain 3-lithiotellurophene **15** by reaction of **7a** with *n*-BuLi at −78 °C. However, **15** was not obtained since opening of the tellurophene ring occurred. That the ring opening occurs after reaction with *n*-BuLi is readily established since the stereochemical pure acyclic ditelluride **14** can be isolated in 54% yield by carrying out the reaction of **7a** with *n*-BuLi (0.75 equiv) at −78 °C (Scheme 2). The corresponding acyclic monotelluride **16** with *Z* configuration at the double bonds was obtained when the reaction was conducted with 2.0 equiv of *n*-BuLi at room temperature. ^{1}H NMR spectral analysis shows a single stereoisomer in each case, and the vinylic proton undergoes a displacement to high field from 7.9 ppm in **7a** to 6.2 ppm in **16** and to 6.0 ppm in **14**.

A mechanism initially proposed to explain the present ring opening considering the obtained products **14** and **16** consists of the first step of a "retro-Michael" reaction

(34) Hallberg, A.; Liljefors, S.; Pedaja, P. *Synth. Commun.* **1981**, *11*, 25.
(35) Paulmier, C.; Pastour, P. *Compt. Rend., Ser. C* **1967**, *265*, 926.
(36) (a) Suginome, H.; Umezawa, S. *Bull. Chem. Soc. Jpn.* **1936**, *11*, 157. (b) Renson, M. Selenium and Tellurium Heterocycles. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd.: New York, 1986; Chapter 13, pp 399−516.
(37) Mack, W. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 896.
(38) (a) Catel, J.-M.; Mahatsekake, C.; Andrieu, C.; Mollier, Y. *Phosphorus Sulfur* **1987**, *34*, 119. (b) Kulik, W.; Verkrüijsse, H. D.; de Jong, R. L. P.; Hommes, H.; Brandsma, L. *Tetrahedron Lett.* **1983**, *24*, 2203.
(39) Kirsch, G.; Cagniant, P.; Cagniant, D.; Backes, C. *Phosphorus Sulfur* **1979**, *6*, 161.
(40) Discordia, R. P.; Dittmer, D. C. *Tetrahedron Lett.* **1988**, *29*, 4923.
(41) Luppold, E.; Müller, E.; Winter, W. *Z. Naturforsch.* **1976**, *31B*, 1654.

Table 2. Results Obtained by Reaction of 7a with *n*-BuLi[a]

entry	*n*-BuLi (equiv)	*T* (°C)	**7a**	**14**	**5a**	**16**
1	0.62[b]	−78 °C	45	55	trace	trace
2	0.75[b]	−78 °C	3	87	5	5
3	1.0[b]	−78 °C		38	62	
4	1.5[b]	−78 °C			85	15
5	1.1[c]	rt	trace	48	20	32
6	1.75[c]	rt			47	53
7	2.0[c]	rt			10	90

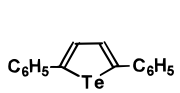
[a] Ratio of products formed determined by ^{1}H NMR. [b] Fast addition of *n*-BuLi. [c] Slow addition of *n*-BuLi.

from a lithium carbanion situated in the β-position to the tellurium atom to give the tellurolate intermediate **17** (Scheme 2). This process is trans-stereospecific giving the *Z* compound, where the triple bond and the Te group are in *cis* positions. A similar ring-opening is known for 3-lithio-2-methylthiophene[42] and for 3-lithio-2,5-dimethylselenophene.[43] However, different products are formed in these cases. In accordance with the classification of a base-induced ring opening of heterocycles previously made,[36b,44] our reaction follows the "ROI" (ring opening type I), which is extended to all eliminative ring openings of β-carbanions.[36b] However, a more detailed study showed that the transformation of **7a** to **17** occurs extremely fast or in a single step, with the cleavage of C(3)−I, C(2)−Te bonds and the triple bond formation occurring probably in a concerted process, since we have not been able to trap with electrophiles the hypothetical intermediate lithium derivative **15** in the same reaction, even at −105 °C.

To establish the second step of the ring-opening mechanism several facts were examined: (a) under an argon atmosphere or air atmosphere, the results of the reaction are similar; (b) only 0.75 equiv of *n*-BuLi are necessary to obtain 100% conversion of **7a** (entry 2; Table 2); (c) the rapid addition (at once) is crucial for the best transformation to **14**. With regard to point a, oxidation of **17** is not necessary to obtain **14** since this reaction gave good results also under an inert atmosphere. As for point b, **7a** ring opening is promoted by *n*-BuLi ("first step", Scheme 2) and also by intermediate **17** ("second step" in Scheme 2). Two different mechanisms were considered for this ring opening promoted by **17**: (1) attack on the tellurium atom of a **7a** could be possible since the iodide is a good leaving group bonded in the β position; (2) attack on the iodo atom of **7a** can also occur considering the great affinity of tellurium for halogen atoms.[37,45] The possibility of tellurophilic reaction (item 1) was eliminated by analysis of two different experiments discussed below. As for point c, slow addition of *n*-BuLi promotes reaction with **14** that is formed before workup, giving other different products, such as **16** and **5a**.

In the second step, the tellurolate anion **17** attacks the iodo atom of a second molecule of **7a** to generate the tellurenyl iodide **8** and another tellurolate anion **17**. These electrophilic (**8**) and nucleophilic (**17**) species react in the last step of the mechanism forming the product **14**.

We believe that the isolation of trace amounts of 2,5-diphenyltellurophene **18** after workup is not indicative that **15** is formed as an intermediate, but that **17** as the intermediate of this ring opening process undergoes an intramolecular attack of tellurolate anion on the triple bond to give the observed compound **18**. Evidence for this was obtained by adding at once 1.5 equiv of *n*-BuLi to **7a** under a completely deoxygenated argon atmosphere at −78 °C. In this case, all **7a** was transformed into **17** by immediate reaction with *n*-BuLi. Water was added under argon and the reaction stirred for an additional 15 min to obtain **18** in 63% yield. The protic medium is necessary for hydrotelluration to occur.



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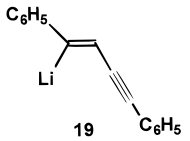
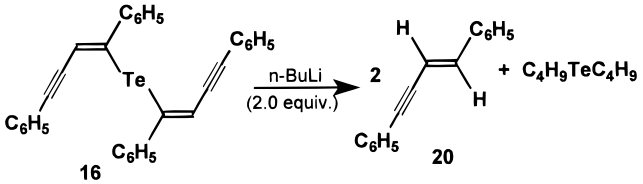


19

When the reaction was carried out by fast addition of *n*-BuLi (0.6 equiv) at −78 °C, 45% of **7a** remained unreacted and **14** was formed (entry 1, Table 2). As shown in Table 2, the best condition to obtain **14** was to use 0.75 equiv of *n*-BuLi (entry 2). If the reaction was performed with 1.0 or 1.5 equiv of *n*-BuLi (entries 3 and 4, Table 2), the principal product formed was **5a**. In one experiment performed as indicated in entry 4 (Table 2) **5a** and **16** were formed in 85:15 ratio as determined by ^{1}H NMR and **5a** was isolated in 65% yield. The last product is formed by the Te−Te bond cleavage of **14** in reaction with butyllithium. The *Z* configuration was attributed to double bonds of compounds **14** and **16**, since reaction of **14** with iodine gives the 3-iodotellurophene (see discussion above) and reaction of **16** with *n*-BuLi (2.0 equiv) resulted in exclusive formation of (*E*)-butenyne **20**.[16] This last reaction could be a valuable alternative



16 **20**

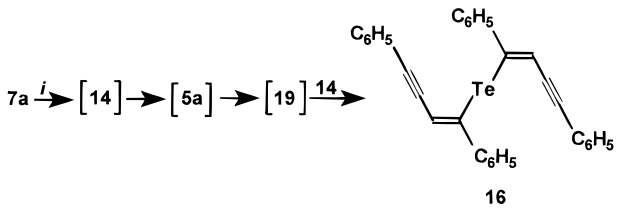
for generating the enynyllithium intermediates. Compound **16** is a source of 2 equiv of the enynyllithium **19**, and the Te/Li exchange reaction occurs with total retention of configuration. Similar results for the Te/Li exchange reaction were previously described for compounds of type **5**,[16] although these compounds furnished only 1 equiv of the enynyllithium.

It was determined by ^{1}H NMR that dropwise addition of *n*-BuLi (2.0 equiv) to a solution of **7a** results in a mixture of **16**, dibutyl telluride, and **5a** as minor product (entry 7, Table 2). The acyclic telluride **16** was isolated as stable yellow crystals (mp = 169−170 °C) in 40% yield by recrystallization from hexane.

The Te/Li exchange reaction of **5a** at room temperature is competitive with the Te−Te bond cleavage in **14**. Consequently, formation of the enynyllithium **19** occurs in the reaction medium. Then, **19** reacts *in situ* with **14** to give **16** by the Te−Te bond cleavage. Compound **16** was prepared independently by reaction of **14** with (1,4-diphenylbut-1-en-3-ynyl)lithium **19** obtained as previously described by us.[16] Proton magnetic resonance and mass spectra as well as the melting point of this sample

(42) Jakobsen, H. *Acta Chem. Scand.* **1970**, *24*, 2663.
(43) Gronowitz, S.; Frejd, T. *Acta Chem. Scand.* **1970**, *24*, 2656.
(44) (a) Gronowitz, S.; Frejd, T. *Chem. Heterocycl. Compd.* **1978**, *14*, 353. (b) Stirling, C. J. M. *Chem. Rev.* **1976**, *32*, 689.
(45) For reviews see: (a) Petragnani, N.; Comasseto, J. V. In *Proceedings of the Fourth International Conference on the Organic Chemistry of Selenium and Tellurium*; Berry, F. J., McWhinie, W. R., Eds.; The University of Aston in Birmingham: Birmingham, 1983; p 97−214. (b) Petragnani, N.; Comasseto, J. V. *Synthesis* **1986**, 1.

Scheme 3[a]

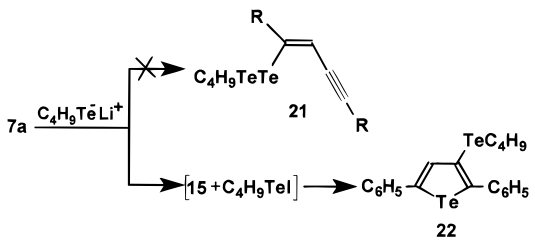


[a] Key: (i) BuLi (2.0 equiv), slow additions, rt.

were indistinguishable from those of **16** obtained by iodotellurophene ring opening (Scheme 3).

Our explanations for the **7a** ring opening to form **14** and **16** are based on attack at the iodine atom by *n*-BuLi in the first step and by tellurolate anion **17** in the second step (Scheme 2). During the early stages of our studies we considered the possibility of an alternative mechanism to the ROI in the formation of **14** or **16** from **7a**. The attack of *n*-BuLi at the tellurium atom and elimination of iodide in the first step were ruled out since formation of the observed compound **14** cannot be explained in this way. However, tellurophilic reactions of **19** or **17** formed as intermediates in the proposed mechanisms (Schemes 2 and 3) with **7a** at the second ring-opening step could be favored by the presence of the good leaving group iodide β to the tellurium atom in **7a**.

This eliminative mechanism called ROII (ring opening type II) was first proposed for the ring-opening product formation of 2,5-dichloro-3-iodoselenophene.[46a] Theoretically, the chalcogenophilic ROII reaction should be easier in **7a** than in selenophenes[46] or thiophenes[47] due to the greater polarizability of the tellurium atom.[42,46,47] However, our experimental results show that the ROII mechanism is not involved in the ring opening of **7a**. The possibility of this tellurophilic mechanism at the second step was eliminated on the basis of two different experiments: (1) Firstly, in the reaction of 0.5 equiv of **19** obtained from **5a** as previously described by us[16] with **7a**, formation of **16** was not observed as principal product as expected by the tellurophilic ring opening (ROII) while formation of 1-iodo-1,4-diphenylbut-1-en-3-yne was detected by CG/MS. (2) Secondly, in the reaction of BuTeLi and **7a** in THF, formation of the unsymmetrical ditelluride **21** expected for a tellurophilic ring-opening was not observed. In the last experiment, the use of 1.0 equiv of BuTeLi resulted in the exclusive formation of the stable 3-(butyltelluro)-2,5-diphenyltellurophene (**22**) in very good yield. We believe that this unexpected product of



the nucleophilic aromatic substitution occurs by the removal of the iodine atom by the butyltellurolate anion furnishing **15** and the butyltellurenyl iodide as intermediates that react immediately to give the observed product **22**.

In conclusion, this work describes the synthesis, reactivity, and mechanistic aspects of the chemistry of several new classes of tellurium compounds such as 3-iodotellurophenes, 3-(butyltelluro)-2,5-diphenyltellurophene, bis-(1,4-diphenyl-1-en-3-ynyl)telluride, and the corresponding ditelluride. We are continuing to explore the scope, limitations, generality, and synthetic applications of these transformations of 3-iodotellurophenes and will report additional findings at a later date.

Experimental Section

General Remarks. ^{1}H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded on a 60 MHz, an 80 MHz, or a 200 MHz spectrometer as noted. CG/MS (using a HP-1 fused silica capillary column) and direct insertion spectra (EI) were measured at 70 eV. 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 are uncorrected. All reactions were 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 without purification was used, and THF was distilled over sodium/benzophenone immediately before use. Dibutyl ditelluride[48] and bis(*p*-methoxyphenyl) ditelluride[49] were prepared by the methods reported in the literature. Compounds **5a**−**f** were obtained as described previously by us.[16]

(*Z*)-1-[(*p*-Methoxyphenyl)telluro]-1,4-diphenyl-1-buten-3-yne (5g). To a solution of 2,4-diphenylbutadiyne (0.606 g, 3.0 mmol) and bis(*p*-methoxyphenyl) ditelluride (0.703 g, 1.5 mmol) in 95% ethanol (20 mL) under N_2 was added sodium borohydride (0.046 g, 1.25 mmol) at room temperature. After disappearance of the red color, the clear yellow mixture was refluxed for 3 h. After workup as described above, the residue was purified by flash chromatography on silica gel with a mixture of hexane:ethyl acetate (9:1) as mobile phase. Evaporation of solvents gave the *p*-methoxytelluro enyne **5g** as a yellow solid, yield 1.050 g (80%). Recrystallized from ethanol: mp 92−93 °C; MS *m*/*z* 440 (23.83) $C_{23}H_{18}TeO$ 310 (57.08), 202 (100.00); 80 MHz ^{1}H NMR ($CDCl_3$) δ 3.63 (s, 3H), 6.41 (s, 1H), 6.56 (d, J = 8 Hz, 2H), 7.0−7.6 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 54.9, 90.0, 97.0, 103.9, 114.9, 115.2, 123.2, 127.6, 127.7, 128.3, 128.5, 131.4, 140.0, 141.4, 159.7. Anal. Calcd for $C_{23}H_{18}TeO$: C, 63.07; H, 4.14. Found: C, 63.01; H, 4.12.

2,5-Diphenyl-3-iodotellurophene (7a). To a one-neck round-bottomed flask containing a solution of (*Z*)-2,4-diphenyl-1-(butyltelluro)-but-1-en-3-yne (**5a**) (0.387 g; 1.0 mmol) in petroleum ether (10 mL) at room temperature was added I_2 (0.507 g, 2.0 mmol) in one portion. The reaction mixture was stirred at this temperature for 1 h 40 min and poured into an Erlenmeyer flask (250 mL). The solid residues were dissolved with ethyl acetate (60 mL), and water (40 mL) was added to the organics. Under vigorous stirring, solid $NaBH_4$ was added in small portions until the dark brown organic phase turned pale yellow (gas evolution is observed). The organic phase was separated and washed with water (4 × 50 mL). After the organic phase was dried over anhydrous $MgSO_4$, the solvents were removed under reduced pressure and the product precipitated. Recrystallization of hexanes gave the pure 3-iodotellurophene **7a** as yellow crystals: 0.379 g (83%); mp = 105−106 °C; MS *m*/*z* 460 (23.18) $C_{16}H_{11}TeI$, 202 (100.00); 80 MHz ^{1}H NMR ($CDCl_3$) δ 7.2−7.6 (m, 10H), 7.9 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 87.5, 126.8, 128.0, 128.2, 128.4, 129.1, 138.5, 141.0, 142.2, 150.1. Anal. Calcd for $C_{16}H_{11}TeI$: C, 41.98; H, 2.42. Found: C, 41.99; H, 2.28.

2,5-Bis(*p*-Methylphenyl)-3-iodotellurophene (7b). The same procedure was followed as for **7a**, using the 2,4-bis(*p*-methylphenyl)but-1-en-3-yne **5b** (0.415g, 1.0 mmol). The

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mixture was stirred for 1.5 h, and after workup, the product **7b** was recrystallized from hexane: yield 0.398 g (82%); MS *m/z* 488 (23.42) $C_{18}H_{15}TeI$, 231 (85.29), 215 (100.00); 80 MHz ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 6H), 7.05 (d, J = 8 Hz, 2H), 7.12 (d, J = 8 Hz, 2H), 7.28 (d, J = 8 Hz, 2H), 7.36 (d, J = 8 Hz, 2H), 7.78 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.2, 21.3, 87.2, 126.5, 128.9, 129.1, 129.7, 135.9, 137.9, 138.2, 141.6, 149.8. Anal. Calcd for $C_{18}H_{15}TeI$: C, 44.50; H, 3.11. Found: C, 44.62; H, 3.14.

2,5-Bis(*p*-methoxyphenyl)-3-iodotellurophene (7c). The same procedure was followed as for **7a**, using the 2,4-bis(*p*-methoxyphenyl)but-1-en-3-yne **5c** (0.447 g, 1.0 mmol). The mixture was stirred for 2 h, and after workup, the product was recrystallized from hexane. Yield: 0.414 g, (80%). MS *m/z* 520 (29.19) $C_{18}H_{15}O_2TeI$, 263 (100.00); 80 MHz ^{1}H NMR ($CDCl_3$) δ 3.79 (s, 3H), 3.81 (s, 3H), 6.82 (d, J = 8 Hz, 2H), 6.88 (d, J = 8 Hz, 2H), 7.32 (d, J = 8 Hz, 2H), 7.43 (d, J = 8 Hz, 2H), 7.72 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 55.2, 55.3, 87.2, 113.8, 114.4, 127.6, 130.3, 131.5, 133.1, 140.7, 141.1, 149.2, 159.3, 159.7. Anal. Calcd for $C_{18}H_{15}OTeI$: C, 41.75; H, 2.92. Found: C, 41.97; H, 2.88.

2,5-Dimethyl-3-iodotellurophene (7d). The same procedure was followed as for **7a**, using the 2,4-dimethylbut-1-en-3-yne **5d** (0.263 g, 1.0 mmol). The mixture was stirred for 3 h, and after workup, the residue was purified by flash chromatography on silica gel with hexane as the mobile phase. After evaporation of hexane, **7d** was obtained as a yellow oil: yield 0.301 g (90%); CG/MS *m/z* 336 (21.44) C_6H_7TeI, 209 (17.60), 77 (100.00); 80 MHz ^{1}H NMR ($CDCl_3$) δ 2.38 (s, 3H), 2.53 (d, $J \approx 1$ Hz, 3H), 7.02 (q, $J \approx 1$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.6, 25.7, 87.8, 135.0, 140.9, 142.5. Anal. Calcd for C_6H_7-TeI: C, 21.60; H, 2.11. Found: C, 21.62; H, 1.98.

3-Iodotellurophene (7e). The same procedure was followed as for **7a**, using the (*Z*)-1-(butyltelluro)but-1-en-3-yne (**5e**) (0.235g, 1.0 mmol). The reaction mixture was stirred for 1 h, and the product was extracted with petroleum ether (3 × 40 mL) and washed with brine (3 × 40 mL). The solid residue (compound **12**) was separated and treated as described below. After evaporation of the petroleum ether layer, the 3-iodotellurophene (**7e**) was obtained as yellow crystals: mp = 37−37.5 °C; yield 0.123 g (40%); CG/MS *m/z* 308 (100.00) C_4H_3TeI, 181 (50.44), 51 (41.12); 80 MHz ^{1}H NMR ($CDCl_3$) δ 7.72 (dd, J = 7 Hz, $J \approx 1.5$ Hz, 1H), 8.60 (dd, J = 7 Hz, $J \approx 2$ Hz, 1H), 8.98 (dd, $J \approx 2$ Hz, $J \approx 1.5$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 85.3, 126.7, 128.2, 145.3. Anal. Calcd for C_4H_3TeI: C, 15.72; H, 0.99. Found: C, 15.75; H, 0.95.

1-(Butyltelluro)-3,4-diiodo-1,3-butadiene (13). To the brown solid residue (containing compound **12**) obtained above that is insoluble in petroleum ether were added tetrahydrofuran (40 mL) and water (30 mL). Under vigorous stirring, solid $NaBH_4$ was added in small portions until the dark brown organic phase turned pale yellow (gas evolution is observed). The organic phase was separated and washed with water (3 × 30 mL). After the organic phase was dried over anhydrous $MgSO_4$, the solvent was removed under reduced pressure. The ^{1}H NMR spectrum of the liquid residue showed that a mixture of **7e** and **13** in a 1:2 ratio was present: 60 MHz ^{1}H NMR of **13** ($CDCl_3$) δ 0.93 (t, J = 7 Hz, 3H), 2.0−3.0 (m, 4H), 2.68 (t, J = 7 Hz, 2H), 6.75 (d, J = 11 Hz, 1H), 7.01 (s, 1H), 7.19 (d, J = 11 Hz, 1H). Attempts to separate **13** by distillation failed since at 84 °C/0.01 mmHg **13** decomposes losing iodine to give compound **5e**.

2-Phenyl-3-iodotellurophene (7f). The same procedure was followed as for **7a**, using the (*Z*)-1-(butyltelluro)-4-phenylbut-1-en-3-yne (**5f**) (0.311 g, 1.0 mmol). The mixture was stirred for 4 h, and after workup, the residue was purified by flash chromatography on silica gel with hexane as mobile phase. After evaporation of hexane **7f** was obtained as a yellow oil: yield 0.305 g (80%); MS *m/z* 384 (0.00) 256 (7.23), 64 (100.00); 80 MHz ^{1}H NMR ($CDCl_3$) δ 7.2−7.6 (m, 5H), 7.87 (d, J = 7 Hz, 1H), 8.69 (d, J = 7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 127.9, 128.3, 129.1, 147.0. Anal. Calcd for $C_{10}H_7TeI$: C, 31.47; H, 1.85. Found: C, 31.28; H, 1.93.

2,3-Diiodotellurophene (7g). The same procedure was followed as for **7e**, except that 0.762 g (3.0 mmol) of iodine was used and the reaction mixture was stirred for 4 h. After treatment with $NaBH_4$ and workup as described above, the residue was distilled in a Kugelrohr apparatus. The compound **7e** was distilled at 105 °C/0.1 mmHg, followed by **7g** (140 °C/0.1 mmHg): yield of **7g** 0.017 g (4%); MS *m/z* 434 (75.84) C_4H_2-TeI_2, 307 (50.18), 127 (100.00); 80 MHz ^{1}H NMR ($CDCl_3$) δ 7.52 (d, J = 7.1 Hz, 1H), 8.87 (d, J = 7.1 Hz, 1H).

2-Phenyl-3-iodotellurophene Diiodide (9a). To a one-neck round-bottomed flask containing a solution of (*Z*)-1-(butyltelluro)-4-phenylbut-1-en-3-yne (**5f**) (0.311 g, 1.0 mmol) in petroleum ether (10 mL) at room temperature was added iodine (0.507 g, 2.0 mmol) in one portion. The reaction mixture was stirred at this temperature for 4 h, extracted with ethyl acetate, and washed with a saturated solution of sodium thiosulfate (4 × 60 mL). After the organic phase ($MgSO_4$) was dried, the solvents were removed under reduced pressure and the residue was recrystallized from carbon tetrachloride to give the pure compound **9a** as highly insoluble yellow-brown crystals 0.283 g (45%): mp = 108−109 °C; MS *m/z* 638 (0.00), 256 (7.1), 64 (100.00); 60 MHz ^{1}H NMR (THF-d_6) δ 7.0−7.5 (m, 5H), 7.76 (d, J = 7 Hz, 1H), 8.77 (d, J = 7 Hz, 1H). Anal. Calcd for $C_{10}H_7TeI_3$: C, 18.82; H, 1.11. Found: C, 18.43; H, 0.97.

Bis(1,4-diphenylbut-1-en-3-ynyl) ditelluride 14. To a two-neck round-bottomed flask, under N_2, containing a solution of **7a** (0.458 g, 1.0 mmol) in THF (10 mL) at −78 °C was added *n*-BuLi (0.3 mL, 0.75 mmol, 2.5 M) in one portion. The initial yellow solution turned dark red. The reaction mixture was stirred for 10 min, and then water (2.0 mL) was added. The reaction mixture was diluted with ethyl acetate (∼40 mL) and washed with brine (3 × 50 mL). The organic phase was dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure, and the dark red residue was purified by flash chromatography to give compound **14** as identified by ^{1}H NMR spectroscopy. Compound **14** is unstable, and elemental analysis was not possible: 0.178 g (54%); MS *m/z* 666 (M + 4) (0.00), 536 (6.34) $C_{32}H_{22}Te$, 406 (36.09), 329 (15.45), 202 (100.00); 60 MHz ^{1}H NMR ($CDCl_3$) δ 6.1 (s, 2H), 7.1−7.7 (m, 20H).

2,5-Diphenyl-3-iodotellurophene (7a) by Reaction of 14 with I_2. To a one-neck round-bottomed flask containing a solution of **14** (0.331 g; 0.5 mmol) in petroleum ether (10 mL) at room temperature was added I_2 (0.254 g; 1.0 mmol) in one portion. The reaction mixture was stirred at this temperature for 1 h, poured into an Erlenmeyer flask (250 mL), and diluted with ethyl acetate (40 mL), and water (40 mL) was added to the organics. Under vigorous stirring, solid $NaBH_4$ was added in small portions until the dark brown color turned pale yellow (gas evolution is observed). The organic phase was separated and washed with water (4 × 50 mL). After the organic phase was dried over anhydrous $MgSO_4$, the solvents were removed under reduced pressure. Recrystallization of hexanes gave the pure 3-iodotellurophene (**7a**) as yellow crystals. Yield: 0.229 g (50%). Physical properties and spectral data are similar to those of compound **7a** obtained by reaction of **5a** with iodine.

Bis(1,4-diphenylbut-1-en-3-ynyl) Telluride (16). To a two-neck round-bottomed flask under deoxygenated nitrogen, containing a solution of **7a** (0.458 g, 1.0 mmol) in THF (10 mL), was added *n*-BuLi (0.8 mL, 2.0 mmol, 2.5 M) dropwise (over 3 min). During the addition the initial yellow solution turned red. After the end of addition (3 min) the reaction mixture was stirred for 30 min (the solution turned yellow again), and then water (2.0 mL) was added under N_2. The reaction mixture was diluted with ethyl acetate (∼40 mL) and washed with brine (3 × 50 mL). The organic phase was dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure, and the yellow solid formed was washed with hexane. The solid was purified by recrystallization from hexane to obtain the pure compound **16**: 0.363 g (68%); mp = 169−170 °C; MS *m/z* 536 (9.03) $C_{32}H_{22}Te$, 406 (56.36), 329 (21.46), 202 (100.00); 200 MHz ^{1}H NMR ($CDCl_3$) δ 6.28 (s, 2H), 7.07 (s,10H), 7.2−7.4 (m, 6H), 7.5−7.7 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 90.8, 117.1, 123.2, 127.6, 127.8, 128.4, 129.6, 131.5, 140.2, 142.0. Anal. Calcd for $C_{32}H_{22}Te$: C, 71.96; H, 4.15. Found: C, 71.56; H, 4.0.

(*E*)-1,4-Diphenyl-1-buten-3-yne (20) by Reaction of 16 with *n*-BuLi. To a solution of **16** (0.267 g, 0.5 mmol) in THF

(5 mL) at room temperature under an atmosphere of nitrogen was added *n*-BuLi (0.5 mL, 1.2 mmol, 2.48 M in hexane) in one portion. The reaction was stirred for 15 min and then treated with a saturated solution of NH_4Cl (3 mL), diluted with ethyl acetate (20 mL), and washed with brine (3 × 15 mL). After the organic phase was dried ($MgSO_4$), the solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel, using hexane as eluent. Hexane was partially evaporated to give white crystals of (*E*)-enyne **20**, yield 0.116 g (82%). Recrystallized from ethanol: mp 96−97 °C (lit.[16a]).

2,5-Diphenyltellurophene 18 by Reaction of 7a with *n*-BuLi. To a two-neck round-bottomed flask, containing a solution of **7a** (0.458 g, 1.0 mmol) in dry THF (10 mL) at −78 °C under an atmosphere of argon, was added *n*-BuLi (0.7 mL, 1.75 mmol, 2.5 M) in one portion. The color changed to dark red during the addition. The mixture was stirred for 10 min, the cooling bath was removed, and water was added (10 mL) under an argon atmosphere. After being warmed to room temperature, the reaction mixture was stirred for 15 additional minutes and then diluted with ethyl acetate (∼50 mL) and washed with brine (3 × 40 mL). The organic phase was dried over anhydrous $MgSO_4$, the solvents were evaporated, and the solid residue was washed with hexane to remove impurities. Recrystallization from chloroform/petroleum ether gave 2,5-diphenyltellurophene **18** as a yellow solid: yield 0.138 g (42%); mp 220−224 °C; MS *m*/*z* 334 (59.90), 203 (100.00); 80 MHz ^{1}H NMR ($CDCl_3$) δ 7.2−7.6 (m, 10H), 7.81 (s, 1H).

2,5-Diphenyl-3-(butyltelluro)tellurophene (22). To a suspension of elemental tellurium (0.255 g, 2.0 mmol) in dry THF (6 mL) under an atmosphere of nitrogen at 0 °C was added *n*-BuLi in hexanes (0.8 mL, 2.0 mmol, 2.5 M). When all tellurium was dissolved, the solution turned yellow green and a solution of **7a** (0.915 g, 2.0 mmol) in THF (4 mL) was added. After the mixture was stirred for an additional 10 min at 0 °C, water (5 mL) was added. The reaction mixture was diluted with ethyl acetate (∼40 mL) and washed with brine (3 × 40 mL). The organic phase was dried over anhydrous $MgSO_4$, the solvents were evaporated under reduced pressure, and the residue was purified by flash chromatography on silica gel using hexane as the mobile phase. After hexane evaporation **22** was obtained as a yellow oil: yield 0.71 g (72%); MS *m*/*z* 518 (7.71) $C_{20}H_{20}Te_2$, 460 (4.55), 332 (12.60), 202 (100.00); 200 MHz ^{1}H NMR ($CDCl_3$) δ 0.81(t, J = 7 Hz, 3H), 1.26 (sext, J = 7 Hz, 2H), 1.64 (quint, J = 7 Hz, 2H), 2.78 (t, J = 7 Hz, 2H), 7.2−7.6 (m, 10H), 7.88 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 8.9, 13.3, 24.8, 33.6, 112.5, 126.8, 127.6, 128.1, 128.8, 139.3, 141.7, 142.7, 150.1. Anal. Calcd for $C_{20}H_{20}Te_2$: C, 46.16; H, 3.88. Found: C, 45.95; H, 3.56.

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Supporting Information Available: Copies of the ^{1}H NMR, ^{13}C NMR, and mass spectra of compounds **5g**, **7a**−**g, 16, 18, 20,** and **22** and ^{1}H NMR for compounds **9a**, **13**, and **14** (37 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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