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Electrotelluration: A New Approach to Tri- and Tetrasubstituted Alkenes

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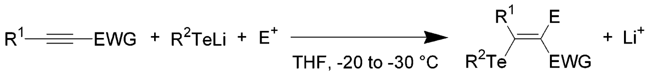
A novel electrotelluration process is described in which a Michael addition of an alkyl or aryl tellurolate anion occurs onto an activated alkyne with subsequent trapping of a vinyl anion with electrophiles (aldehydes and ketones) other than a proton. This process provides an efficient regio- and stereospecific route to tri- and tetrasubstituted alkenes. Methodologically significant examples of this chemistry were studied in which aryl and alkyl tellurolate anions were added to ω-keto alkynyl esters in a Michael reaction, and the incipient vinyl anions were trapped intramolecularly by the internal aldehydes. The reactive centers were tethered by different lengths of alkyl chains to form highly functionalized five-, six-, seven-, and eight-membered rings in modest to good yields.

Introduction

Hydrometalation reactions of alkynes such as hydroalumination,[1] hydroboration,[2] and hydrozirconation[3] provide direct routes to *E*-alkenylorganometallics which can be further utilized to make carbon−carbon bonds via transmetalation/cross-coupling[4] reactions. In contrast to the above hydrometalation reactions, hydrotelluration reactions lead to exclusively a *Z*-alkene,[5−8] thus providing a unique route to organometallics with opposite stereochemistry.

In hydrotelluration reactions,[5−8] we anticipated that a vinyl anion intermediate was formed and sequentially trapped by a proton. In an effort to expand the scope of the hydrotelluration reactions to include other electrophiles, we set out to trap the “vinyl anion intermediate” with electrophiles such as aldehydes, ketones, and trialkylsilyl chlorides (Scheme 1). The expected product would be a tri- or tetrasubstituted alkene (depending on whether one starts with a mono- or disubstituted alkyne) bearing a vinylic telluride that could be further transmetalated to lithium,[9] copper,[10] or zinc[11] to perform other carbon−carbon bond forming reactions. Vinylic tellurides can also undergo cross-coupling reactions directly with terminal alkynes,[12] alkylzinc,[13] alkynylzinc,[14] and Grignard reagents[7] or react with carbon monoxide[15] catalyzed by a transition metal. These stereodefined tri- or tetrasubstituted alkenes bearing vinylic tellurides can be important precursors for the synthesis of natural products containing alkenes and polyenes.[16] Several successful trapping experiments using tellurolate anions are reported herein.

SCHEME 1. The Electrotelluration Reaction



EWG = electron withdrawing groups (esters, sulfoxides, and sulfones)
R^2 = *n*-Bu, Ph; E^+ = aldehydes, ketones

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SCHEME 2. Deuteration Experiments

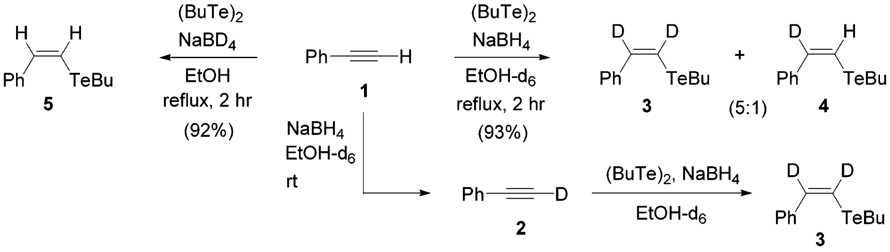
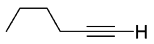
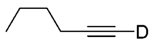
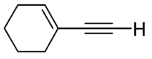
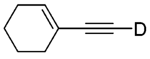
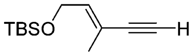
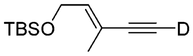


TABLE 1. H−D Exchange Reaction

Entry[a]	Starting Alkyne (A)	Product (B)		Ratio of A:B after 1 hr[b]	Ratio of A:B after 12 hr[b]
1	Ph—≡—H	Ph—≡—D	(**2**)	1.4 : 1	1 : 15
2			(**6**)	6 : 1	1 : 9.5
3			(**7**)	1.1 : 1	1 : 11.6
4			(**8**)	1 : 6.4	1 : 19.4

[a] All reactions were performed at room temperature in a NMR tube using alkyne (1 equiv), NaBH$_4$ (1 equiv) in EtOH-d$_6$.
[b] ^{1}H NMR ratio of the reaction mixture.

Results and Discussion

In the hydrotelluration process leading to a *Z*-alkene exclusively, the alkyl tellurolate anion and the hydrogen are known to add to the alkyne in a *trans*-fashion. The proton is believed to come from the hydroxy group of ethanol. We decided to design deuteration experiments to confirm that the hydrogen came from the alcohol rather than from sodium borohydride (Scheme 2). As anticipated, upon treatment of phenyl acetylene with dibutyl ditelluride in the present of sodium borodeuteride and ethanol, we did not obtain any deuterated product (**1** to **5**). On the other hand, both a monodeuterated alkene (**4**, expected) and a dideuterated alkene (**3**) were detected if we used sodium borohydride and deuterated ethanol. We believe that the dideuterated product (**3**) must come from the deuterated phenyl acetylene that subsequently undergoes the deuteriotelluration reaction. In fact, upon treatment of phenyl acetylene with sodium borohydride and deuterated ethanol at room temperature, the alkynyl hydrogen exchanged with the deuterium in a few hours (Scheme 2, **1** to **2**; Table 1, entry 1). In addition, we found that 1-hexyne (entry 2) and enynes (entries 3 and 4) also underwent the alkynyl hydrogen−deuterium exchange reaction. Since the deuteration experiments conclusively establish the source of the *trans*-hydrogen to be from the protic solvent rather than from the hydridic NaBH$_4$, it is anticipated that replacement of ethanol with more elaborate electrophiles can extend the scope of the hydrotelluration reaction to a more general electrotelluration reaction. This requires generation of the tellurolate anions in aprotic solvent under different conditions, such as elemental tellurium and *n*-BuLi[17] or PhLi[18] in THF rather than sodium borohydride in ethanol.

Our initial attempts at the electrotelluration process were performed using phenylacetylene and (*E*)-5-[(1,1-dimethylethyl)dimethylsilyloxy]pent-3-en-1-yne which are known substrates for the hydrotelluration reaction;[8] however, after exploring various reaction conditions (varying time and temperature), we did not obtain any trapping of benzaldehyde. At this stage, attention was focused on more activated alkynes bearing electron-withdrawing groups (i.e., ester, sulfone, and sulfoxide), since alkynyl esters are also known substrates for the hydrotelluration reaction.[19] In addition, thiolate anions can add to activated alkynes, and the incipient vinyl anions can be intercepted with aldehydes or ketones.[20] We began with methyl propiolate, a terminal acetylenic ester, as our Michael acceptor. As expected, the electrotelluration reaction proceeded smoothly between −20 to −30 °C in 5 min (stoichiometric amounts of the nucleophile, Michael acceptor, and electrophile were used in all of the experiments) affording the trapping products (Table 2). Different combinations of electrophiles (benzaldehyde and *n*-butyraldehyde) and nucleophiles (lithium *n*-butyl and phenyl tellurolate) worked well. In addition, TMSCl (entry 5) was also trapped by the "vinyl anion". ^{1}H NMR of the crude reaction mixture showed that only one isomer was formed and no O-silylation product was present. NOE experiments showed an enhancement of the carbinol hydrogen when the vinyl hydrogen was irradiated confirming the trans-addition of the electrotelluration (entries 1 and 2). We believe that the trans-

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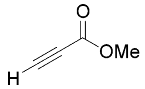
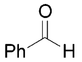
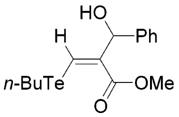
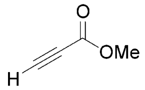
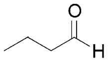
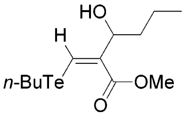
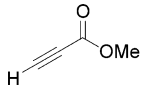
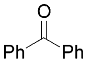
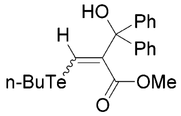
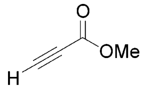
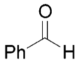
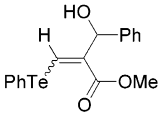
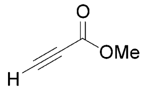
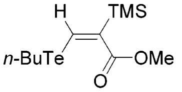
TABLE 2. Acetylenic Esters in the Electrotelluration

Entry[a]	Alkyne	Nucleophile	Electrophile	Product		Time	Temperature	Yield	*E:Z*
1		*n*-BuTeLi			(**9**)	10 min	-30 °C	71	*Z* only
2		*n*-BuTeLi			(**10**)	10 min	-20 °C	46	*Z* only
3		*n*-BuTeLi			(**11**)	10 min	-30 °C	43	1:3
4		PhTeLi			(**12**)	10 min	-30 °C	84	1:13
5		*n*-BuTeLi	TMSCl		(**13**)	20 min	-20 °C	45	*E* only

[a] All reactions were performed in THF using stoichiometric amounts of alkyne, nucleophile and electrophile.

addition was also operable in entries 3 and 4 with the following reaction profile. In the case of 3, the less reactive ketone (benzophenone) allowed cis−trans equilibration of the "vinyl anion". Lithium phenyl tellurolate is less reactive than lithium *n*-butyl tellurolate, thus allowing the incipient vinyl anion to also equilibrate (entry 4). The electrotelluration failed if alkyl halides and epoxides were used because tellurolate anions reacted with these electrophiles much faster than with methyl propiolate.

Stemming from the success of the terminal acetylenic ester as an efficient Michael acceptor in the electrotelluration reaction, we decided to expand the scope to activated alkynes bearing sulfone and sulfoxide (Table 3). Nonterminal acetylenic sulfones and sulfoxides (entries 1 to 5) readily underwent the electrotelluration affording functionalized, stereodefined tetrasubstituted alkenes (**14** to **18**). Analogous to the acetylenic esters, lithium tellurolate anions and electrophiles were added to acetylenic sulfones and sulfoxides in a trans-fashion giving *Z*-isomers exclusively. We decided to explore alkynyl sulfides in the electrotelluration because the resulting vinylic sulfide can be used in cross-coupling reaction with Grignard reagents.[21] Nonterminal alkynyl sulfide (entry 6) did not undergo the electrotelluration process under a variety of conditions. However, a terminal alkynyl sulfide (entry 7) underwent the electrotelluration at a higher temperature and a longer reaction time compared to the alkynyl sulfones and sulfoxides affording exclusively a trans-addition product (**19**). From these results, we can conclude that first, the terminal acetylenic sulfide is more reactive than the corresponding nonterminal acetylenic sulfide due to steric effects (entry 6 vs 7); and second, the nonterminal acetylenic sulfones and sulfoxides are more reactive Michael acceptors than the corresponding nonterminal acetylenic sulfide (entries 1 to 5 vs 6) due to electronic effects.

From the intermolecular trapping experiments described above, one can conclude that the tellurolate anions react with activated alkynes faster than they react irreversibly with the trapping electrophiles. This compatibility of functionality suggests the possibility of carrying out an intramolecular version of the electrotelluration reaction. We anticipated that by tethering the Michael acceptors and the electrophiles, we can effect the intramolecular version of the electrotelluration process, and the results are reported herein. The present proposal is analogous to an intramolecular Baylis−Hillman reaction[22] in which we employ tellurolate anions instead of amine[23] or phosphine[24] nucleophiles to promote the ring formations. The advantage of incorporation of the tellurium nucleophile into the intramolecular electrotelluration product is that it can be transformed into Li,[9] Cu,[10] and Zn[11] or cross-couple with terminal alkynes,[12] alkylzinc,[13] alkynylzinc,[14] Grignard reagents,[7] or react with carbon monoxide[15] catalyzed by transition metals.

To test the hypothesis, we designed suitable substrates that should be reactive and yet could be obtained easily in high yield for the study. We synthesized alkynyl esters bearing a reactive aldehyde group tethering with chains of different carbon lengths to form different ring systems. While the starting materials 4-pentyn-1-ol (**20a**) and 5-hexyn-1-ol (**20b**) for the construction of five- and six-membered rings respectively were commercially avail-

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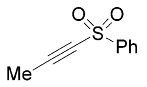
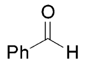
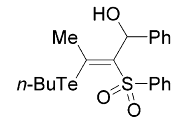
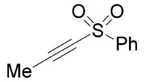
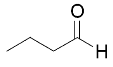
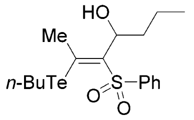
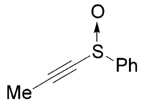
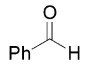
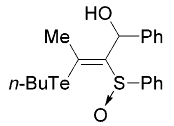
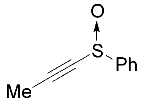
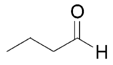
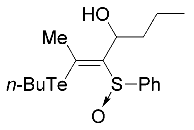
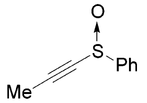
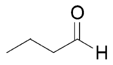
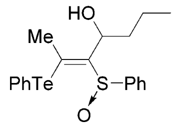
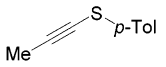
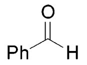
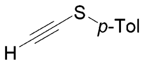
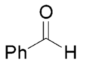
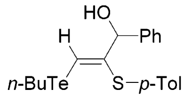
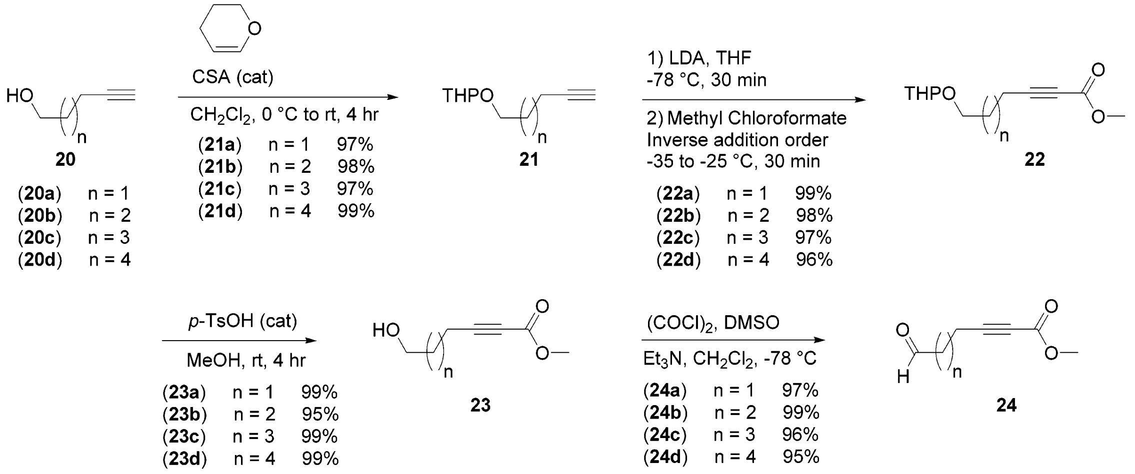
TABLE 3. Acetylenic Sulfones, Sulfoxides, and Sulfides in the Electrotelluration

Entry[a]	Alkyne	Nucleophile	Electrophile	Product	Time	Temperature	Yield	*E*:*Z*
1		*n*-BuTeLi		 (**14**)	5 min	-20 °C	69	*Z* only
2		*n*-BuTeLi		 (**15**)	5 min	-30 °C	60	*Z* only
3		*n*-BuTeLi		 (**16**)	10 min	-30 °C	65[b]	*Z* only
4		*n*-BuTeLi		 (**17**)	5 min	-30 °C	67[b]	*Z* only
5		PhTeLi		 (**18**)	10 min	-30 °C	78[b]	*Z* only
6		*n*-BuTeLi		no product	24 hr	-20 °C to rt		
7		*n*-BuTeLi		 (**19**)	15 min	0 °C	56	*Z* only

[a] All reactions were performed in THF using stoichiometric amounts of alkyne, nucleophile and electrophile.

[b] mixture of diastereomers with *Z*-configuration.

SCHEME 3. ω-Keto Alkynyl Esters Syntheses



able, 6-heptyn-1-ol (**20c**) and 7-octyn-1-ol (**20d**) were prepared in two steps[25] from propargyl alcohol and 1-bromobutane and 1-bromopentane, respectively.

Initially, we protected the alcohol of 5-hexyn-1-ol as a TBS ether.[26] However, the subsequent acylation step gave a low yield (ca. 40%) of the alkynyl ester despite several attempts. We switch the protecting group to THP which has been known to be very stable toward basic conditions (Scheme 3). THP protection of the alkynyl alcohol **20b** followed by the formation of the alkynyl acetylide with LDA and subsequent acylation with methyl chloroformate proceeded in high yield.[27] Normal addition of methyl chloroformate to the alkynyl acetylide[28] gave a much

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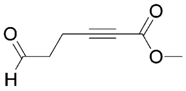
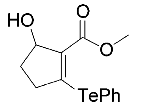
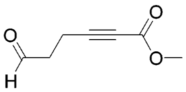
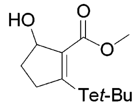
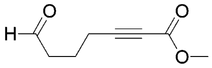
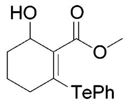
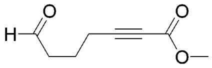
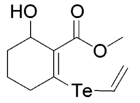
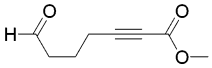
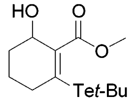
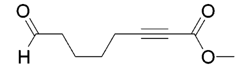
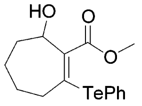
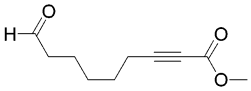
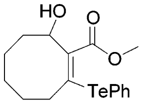
[25] (a) Brandsma, L.; Verkruijsse, H. D. In *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: New York, 1981; p 77. (b) Huang, H.; Forsyth, C. J. *J. Org. Chem.* **1997**, *62*, 8595−8599. (c) Ma, D.; Lu, X. T. *Tetrahedron* **1990**, *46*, 6319−6330.

[26] (a) Kalivretonos, A.; Stille, J. K.; Hegedus, L. S. *J. Org. Chem.* **1991**, *56*, 2883−2894. (b) Nystrom, J.-E.; McCanna, T. D.; Helquist, P.; Amourouse, R. *Synthesis* **1988**, 56−58.

TABLE 4. Intramolecular Electrotelluration Results

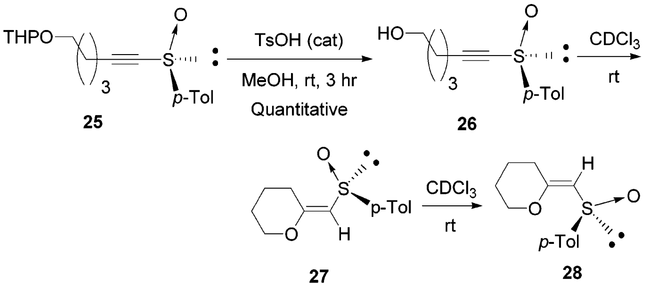
Entry[a]	Michael Acceptor	Nucleophile	Product	Yield
1		PhTeLi	 (**29**)	72
2		*t*-BuTeLi	 (**30**)	51
3 a)		PhTeLi	 (**31**)	80
b)		PhTeMgBr (1 equiv)		51
c)		PhTeMgBr (2 equiv)		79
4			 (**32**)	74
5		*t*-BuTeLi	 (**33**)	31
6 a)		PhTeLi	 (**34**)	41
b)		PhTeMgBr (1 equiv)		30
7		PhTeLi	 (**35**)	48

[a] All reactions were performed in THF at room temperature using stoichiometric amounts of Michael acceptor and nucleophile unless indicated otherwise.

lower yield than the inverse addition order. Dropwise addition of the acetylide anions to a vigorously stirred and freshly distilled methyl chloroformate solution provided alkynyl ester **22b** in high yield.[29] THP deprotection with catalytic amount of *p*-toluenesulfonic acid in methanol[27] followed by Swern oxidation[28,30] provided alkynyl ester bearing the aldehyde **24b** in high yield.[28] Intermediates **23** and **24** were isolated and quite stable when stored at 0 °C. During the THP deprotection and Swern oxidation, we did not detect any ring closing product as a consequence of a possible intramolecular Michael addition of the alcohol to the alkynyl ester. Similarly, five-, seven-, and eight-membered ring substrates (**24a**, **24c**, and **24d**) were made also in high overall yields (Scheme 3; $n = 1$, 3, and 4) in four chemical steps from the alkynyl alcohols (**20a**, **20c**, and **20d**).

In contrast, the alkynyl sulfoxide substrate could not be made in this manner because it is a better Michael acceptor than the alkynyl ester. During the alcohol deprotection of alkynyl sulfoxide substrate, we obtained the ring-closing product (Scheme 4, **26**), formed by the intramolecular Michael addition of the alcohol to the alkynyl sulfoxide. The *E*-isomer **27** was unstable and isomerized to the *Z*-isomer **28** after several hours in the NMR tube.

SCHEME 4. Intramolecular Michael Addition during the Synthesis of Alkynyl Sulfoxide Substrate



after 7 hr, 26 : 27 : 28 is 5.1 : 1.5 :1
after 19 hr, only 28

With the appropriate alkynyl esters in hand, we decided to test the intramolecular electrotelluration. Treatment of a stoichiometric amount of alkynyl ester **24b** ($R_f = 0.47$ in 65:35 Hex:EtAc) and lithium *n*-butyl tellurolate in THF at room temperature under high dilution conditions (0.05 M) afforded a single compound that showed up on TLC as a bright yellow spot ($R_f = 0.39$ in 65:35 Hex:EtAc) with iodine detection, a normal characteristic of a vinylic telluride. After a normal

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(27) Kita, Y.; Okunaka, R.; Honda, T.; Shindo, M.; Taniguchi, M.; Kondo, M.; Sasho, M. *J. Org. Chem.* **1991**, *56*, 119–125.

(28) Trost, B. M.; Shi, Y. *J. Am. Chem. Soc.* **1993**, *115*, 12491–12509.

(29) Brandsma, L. In *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, 1988; p 101.

(30) (a) Manucuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480–2482. (b) Omura, K.; Swern, D. *Tetrahedron* **1978**, *34*, 1651–1660.

workup and flash column chromatography on silica gel, the product was isolated but there were signs of decomposition according to TLC and NMR analyses. We believe that the expected product was produced but it was oxidized to telluroxide and tellurone during the chromatography. To further confirm our expectation, GC-MS analysis of the samples after chromatography indicated a major peak correspond to the tellurone product ($m/z = 372$, any telluride and telluroxide in the mixture was likely oxidized to tellurone during GC-MS acquisition).

From these preliminary results, we learned that the intramolecular electrotelluration with *n*-butyl tellurolate anion did work but the product was quickly oxidized. To circumvent this problem, we turn our attention to lithium phenyl tellurolate anion because from our experience and others,[31] aryl telluroalkenes are more stable toward oxidation than alkyl telluroalkenes. As expected, lithium phenyl tellurolate anion participated in the intramolecular electrotelluration affording products (**29**, **31**, **34**, and **35**) that were much more air stable and were isolated by flash column chromatography on silica gel (Table 4; entries 1, 3a, 6a, and 7). The intramolecular electrotelluration was complete between 5 to 10 min at room temperature, affording different ring systems in modest to good yield with different functional groups such as the allylic alcohol, the ester, and the vinylic telluride. Eight- and seven-membered rings (entries 6 and 7) were obtained in much lower yield because the proton trapping of the vinyl anion intermediate was competitive with the intramolecular cyclization. ^{1}H NMR showed the crude product to be 10−20% proton-trapped product in these cases. In addition, no intermolecular electrotelluration product was detected under the high dilution condition.

Knowing that the phenyl group can stabilize the tellurium atom toward oxidation by electronic effects, we decided to test if a *tert*-butyl group can stabilize the tellurium atom by a steric effect. The lithium *tert*-butyl tellurolate underwent the intramolecular electrotelluration in moderate yield (entries 2 and 5) that indicated the *tert*-butyl group did not stabilize the tellurium atom as well compared to the phenyl group. Instead of the lithium phenyl tellurolate anion, a magnesium phenyl tellurolate anion also worked but in lower yields (entries 3a and 6b) because the insertion of the elemental tellurium into the phenyl−magnesium bond was incomplete.[32] Experimentally, the elemental tellurium remained regardless of the prolong heating with phenylmagnesium bromide in refluxing THF. The yield was improved when 2 equiv of the magnesium phenyl tellurolate was employed (entry 3c). In addition, a magnesium vinyl tellurolate[5,33] also underwent the intramolecular electrotelluration process in modest yield (entry 4). From this study, since lower reaction yields are found to be directly related to the ease of telluride oxidation, the relative stability of cyclic vinylic tellurides toward air is as follows: PhTe > vinylTe ∼ *t*-BuTe > *n*-BuTe. Furthermore, the preliminary results suggest that the identity of the tellurolate counterion is not highly relevant to the overall reaction.

Conclusions

This is the first reported Michael addition of tellurolate anions to activated alkynes followed by the trapping of the incipient “vinyllithium” by electrophiles other than a proton source. The electrotelluration essentially expands the scope of the hydrotelluration because one can obtain highly functionalized tri- or tetrasubstituted alkenes containing vinylic tellurides and vinyl sulfides, sulfoxides, or sulfones that can be used for other carbon−carbon bond forming reactions. For instance, vinylic sulfides can be cross-coupled with Grignard reagents[21] catalyzed by Ni-catalyst while vinylic sulfoxides can be elaborated to lactones.[34] We propose that a vinyllithium intermediate is formed and sequentially trapped by the electrophiles. This proposal would be the starting point for further studies to elucidate the mechanism of the hydrotelluration and the electrotelluration reaction.

Acknowledgment. This work was supported by the University of Michigan. We thank Professor Miguel J. Dabdoub (Universidade de São Paulo, Ribeirão Preto, Brazil) for insightful discussion and suggestions.

Supporting Information Available: Sample procedure for the electrotelluration and characterization data (^{1}H NMR, ^{13}C NMR, NOE, FTIR, and HRMS) for all compounds are available free of charge via the Internet at http://pubs.acs.org.

JO0110146

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[31] Engman, L.; Stern, D. *Organometallics* **1993**, *12*, 1445−1448.

[32] (a) Haller, W. S.; Irgolic, K. J. *J. Organomet. Chem.* **1972**, *38*, 97−103. (b) Kemmit, T.; Levason, W. *Organometallics* **1989**, *8*, 1303−1308. (c) Petragnani, N.; Campos, M. d. M. *Chem. Ber.* **1963**, *96*, 249−252.

[33] (a) Dabdoub, M. J.; Comasseto, J. V. *J. Organomet. Chem.* **1988**, *344*, 167−173. (b) Petragnani, N. In *Tellurium in Organic Synthesis*; Academic Press: London, 1994; p 72.

[34] (a) Marino, J. P.; Neisser, M. *J. Am. Chem. Soc.* **1981**, *103*, 7687−7689. (b) Marino, J. P.; Perez, A. D. *J. Am. Chem. Soc.* **1984**, *106*, 7643−7644. (c) Marino, J. P.; Fernandez de la Pradilla, R. *Tetrahedron Lett.* **1985**, *26*, 5381−5384. (d) Marino, J. P.; Fernandez de la Pradilla, R.; Laborde, E. *Synthesis* **1987**, 1088−1091. (e) Marino, J. P.; Bogdan, S.; Kimura, K. *J. Am. Chem. Soc.* **1992**, *114*, 5566−5572.