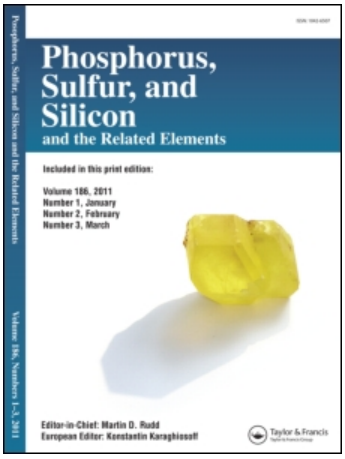

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Braga, Antonio L. , Silveira, ClÁUdio C. , Dornelles, Luciano , Petragnani, Nicola and Stefani, HÉLio A.(2001) 'Addition of Organotellurenyl Bromide to Terminal Acetylenes', Phosphorus, Sulfur, and Silicon and the Related Elements, 172: 1, 181 — 188
To link to this Article: DOI: 10.1080/10426500108046649
URL: http://dx.doi.org/10.1080/10426500108046649

Phosphorus, Sulfur and Silicon, 2001, Vol. 172, pp. 181-188
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Addition of Organotellurenyl Bromide to Terminal Acetylenes

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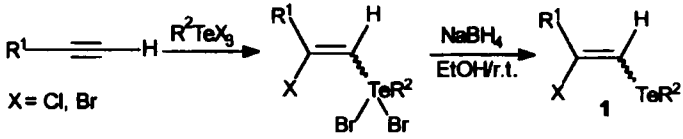
The addition of organotellurenyl bromide to terminal acetylenes promoted by $ZnBr_2$ gives the corresponding β-bromovinylic tellurides preferentially with *E* configuration.

Keywords: vinylic tellurides; organotellurenyl bromide; zinc bromide; tellurium

INTRODUCTION

A number of useful functional group transformations can be achieved by the introduction and sequential manipulation of a tellurium

function.[1] β-Halovinylic tellurides **1** combine the potential of carbon-carbon bond-forming reactions of the vinyl group with the well known transformations of halo compounds.[2] However, these compounds are poorly studied and few methods for their preparation are known. The most convenient consisted of two steps, the addition of organyltellurium trichlorides[3] or tribromides[4,5] to terminal acetylenes, followed by reduction of the corresponding dihalides with $NaBH_4$, as shown in Scheme **1**.



SCHEME 1

In this paper we describe an useful approach to this class of compounds by a direct addition of organotellurenyl bromides to terminal acetylenes. This method avoids the previous preparation, isolation and purification of the corresponding organotellurium dihalides.

RESULTS AND DISCUSSION

Our study began with the reaction of heptyne with phenyltellurenyl bromide in the presence of Lewis acids in THF as the solvent. Zinc bromide ($ZnBr_2$) is the most effective catalyst of several

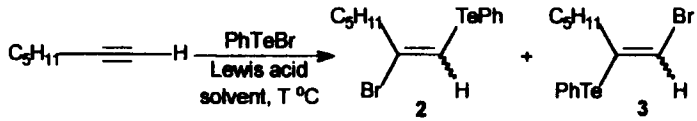
Lewis acids tried. It's application provides the corresponding β-bromovinylic tellurides in satisfactory yields as shown in table 1. With other Lewis acids such as $ZnCl_2$, $HgCl_2$, $HgBr_2$, or $AlCl_3$ lower yields were observed. At room temperature, 33% yield of a 4.3:1 E/Z isomeric mixture of regiosomer **2** was obtained (run 3). When the reaction was conduct at reflux, the yield was improved, however, compound **2** was accompained by its regioisomer (**3**, *E*:*Z* = 2:1, run 5).

We also examined the behavior of other solvent systems (benzene, ethanol, hexane, chloroform) under the same experimental conditions, but only THF was able to promote the addition efficiently. Although the yields and reaction times in THF and benzene were similar (see entry 4 and 7), THF is the solvent of choice allowing an easier isolation of the products.

Regarding the stereochemistry of the formation of **2**, small differences were observed between the systems studied. The *E*-isomer was the major product in most cases. Only the use of higher temperature (refluxing THF or ethanol) promote the predominant formation of the *Z*-isomer, together with a small amount of regioisomer **3**.

Table 2 summarized the results of the reactions of R^2TeBr with several terminal acetylenes. It should be noted that the *E* isomer was obtained preferentially when phenylacetylene, heptyne and acetylene were used, while the exclusive formation of the *E* regioisomer **3** was observed in the reaction with propargyl alcohol. The reactions described were performed very easily by simply mixing all reagents at 50°C.

TABLE 1. Optimization of the Addition of Phenyltellurenyl bromide to Heptyne.



run	Lewis acid	solvent	T (°C)	t (h)	result 2-*Z* 2-*E*	Yield (%)
1	-	THF	r.t.[b]	48	1.0 : 3.6	18
2	-	THF	50	30	1.0 : 3.8	20
3	$ZnBr_2$	THF	r.t.	48	1.0 : 4.3	33
4	$ZnBr_2$	THF	50	24	1.0 : 4.5	50
5	$ZnBr_2$	THF	reflux	18	2.6 : 1.0	62[a]
6	$ZnBr_2$	benzene	r.t.	46	1.0 : 4.0	45
7	$ZnBr_2$	benzene	50	24	1.0 : 4.2	48
8	$ZnBr_2$	ethanol	r.t.	46	1.0 : 3.5	15
9	$ZnBr_2$	ethanol	reflux	24	1.5 : 1.0	49
10	$ZnBr_2$	hexane	50	24	1.1 : 1.0	25
11	$ZnBr_2$	chloroform	50	24	1.0 : 3.8	43

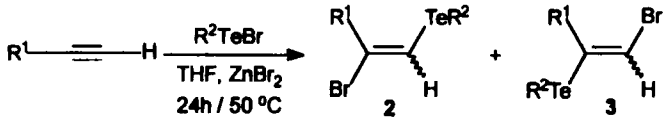
a) Regioisomer **3** was isolated in 13% yield as a mixture of *E*:*Z* = 2:1

b) r.t. = room temperature

The stereochemistry of the *β*-bromovinyl tellurides **2** was established by ^{1}H NMR by comparison with literature[4] data. The preferred *E* geometry of the products suggests that the reaction occurs through a *trans* addition involving a three-centered cyclic transition state. The absolute configuration of **3**-*E* was determined by X-ray

analysis of the crystalline dihalo derivative, obtained by halogenation of the compound 3-*E* (R^2= Ph).[6]

TABLE 2. Preparation of β-Bromovinylic tellurides **2** and **3**.



run	R^1	R^2	2 (%), *Z* : *E*	3*E* (%)
1	C_5H_{11}	Ph	50, 1.0:4.5[a]	-
2	Ph	Ph	20, 1.0:3.5[b]	-
3	H	Ph	20, 1.0:5.3[a]	-
4	CH_2OH	Ph	-	55
5	CH_2OH	*n*-Bu	-	20

a) The *E*:*Z* ratio determined by ^{1}H NMR.

b) *E*:*Z* ratio determined by GC.

EXPERIMENTAL

General: ^{1}H NMR spectra were recorded on a Bruker DPX-200 (200MHz) spectrometer. ^{13}C NMR spectra were obtained on a Bruker DPX-400 (400MHz). IR spectra were recorded on a Perkin Elmer 599-B spectrometer. Elemental analyses were performed at the Microanalytical Laboratory of the Institute of Chemistry – USP. The products and starting materials were analyzed on a Shimadzu 14B chromatograph with a flame-ionization detector.

Column chromatography was carried out with Merck silica-gel (230-400 mesh) according to the procedure by Still and coworkers.[7] Thin layer chromatography (TLC) was performed on silica-gel 60 F-254. All solvents used were previously dried and distilled according to the usual methods.[8] THF was distilled from sodium/benzophenone under N_2, immediately before use. Tellurium metal (320 mesh) and zinc bromide were purchased from Aldrich. The remaining chemicals were obtained from commercial sources. All operations were carried out in flame dried glassware, under an inert atmosphere of dry and deoxygenated N_2. Diphenyl ditelluride[9] and dibutyl ditelluride[10] were prepared by described methods.

Addition of Organotellurenyl bromide to Terminal Acetylenes – Typical Procedure

Organotellurium bromide (1.0 mmol) in CCl_4 (1.0 mL) was added, at room temperature under argon, to a suspension of terminal acetylene (3.0 mmol) and zinc bromide (0.1 mmol) in THF (3.0 mL). The resulting suspension was stirred at 50°C for 24 h and the progress of the reaction was monitored by TLC. After this time, the reaction mixture was cooled to room temperature, dilluted with dichloromethane (15 mL), the organic phase was washed with satured aq. NH_4Cl solution and dried over $MgSO_4$. The solvent was evaporated under vacuum and the residue was purified by flash chromatography on silica gel eluting first with hexane and then with a mixture of hexane/ethyl acetate (9:1).

β-Bromovinylic tellurides **2**:

(*E*/*Z*)-2-Bromo-1-(tellurophenyl)-1-heptene: 200 MHz ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 7.2 Hz, 3H); 1.22-1.33 (m, 2H); 1.47-1.58 (m, 4H); 2.45 (t, J = 7.6 Hz, 2H); 2.53 (t, J = 7.6 Hz, 2H); 6.57 (t, J = 0.8 Hz, 1H); 7.05 (t, J = 1.2 Hz, 1H); 7.20-7.33 (m, 3H); 7.76 (d, J = 6.5 Hz, 2H). 100 MHz ^{13}C NMR ($CDCl_3$) δ 13.88; 22.28; 28.27; 31.12; 33.74; 37.93; 106.75; 108.10; 113.99; 122.97; 130.44; 132.17; 135.62; 137.33; 141.62. IR (neat) ν_{max} (cm-1): 2921; 2856; 1574; 1473; 1434; 1242; 1018; 998; 733; 690.

(*E*/*Z*)-2-Bromo-1-(tellurophenyl)-2-phenylethene: 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.22-7.50 (m, 8H); 7.38 (s, 1H); 7.77 (s, 1H); 7.86 (d, J = 6.5 Hz, 2H). 100 MHz ^{13}C NMR ($CDCl_3$) δ 107.07; 113.74; 114.53; 126.91; 128.26; 128.43; 128.51; 129.24; 129.64; 129.93; 137.57; 138.28; 138.87; 139.42. IR (neat) ν_{max} (cm-1): 3051; 1573; 1474; 1433; 1209; 1017; 997; 867; 732; 691.

(*E*/*Z*)-2-Bromo-1-(tellurophenyl)-1-ethene: 200 MHz ^{1}H NMR ($CDCl_3$) δ 6.51(d, J =14.2 Hz, 1H); 7.15-7.34 (m, 2H); 7.50 (d, J = 14.2 Hz, 1H); 7.60-7.74 (m, 2H). 100 MHz ^{13}C NMR ($CDCl_3$) δ 103.69; 111.07; 112.18; 127.77; 129.12; 130.11; 137.52.

β-Bromovinylic tellurides **3**:

(*E*)-3-Bromo-2-(tellurophenyl)-2-propen-1-ol: Anal. Calcd. for C_9H_9TeOBr: C, 31.73; H, 2.66. Found: C, 31.82; H, 2.55. 200 MHz ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 1H); 4.40 (d, J = 1.2 Hz 2H,); 6.12 (t, J = 1.6 Hz, 1H); 7.21-7.33 (m, 3H); 7.78 (d, J = 6.5 Hz, 2H). 400 MHz ^{13}C

NMR ($CDCl_3$) δ 65.35; 103.78; 112.37; 125.75; 128.43; 129.45; 139.58. IR (neat) ν_{max} (cm-1): 3373; 3065; 2908; 1574; 1474; 1434; 1242; 1047; 1017; 734; 691.

(*E*) 3-Bromo-2-(tellurobutyl)-2-propen-1-ol: 200 MHz ^1H NMR ($CDCl_3$) δ 0.94 (t, J = 7.0 Hz, 2H); 1.36-1.45 (m, 2H); 1.80-1.87 (m, 2H); 2.76 (t, J = 7.6 Hz, 2H); 4.28 (s, 2H); 4.73 (s, 1 OH); 6.50 (t, J = 1.2 Hz, 1H). 100 MHz ^{13}C NMR ($CDCl_3$) δ 8.25; 13.38; 25.01; 33.50; 66.06; 106.75; 121.66. IR (neat) ν_{max} (cm-1): 3409; 2923; 1729; 1450; 1376; 1248; 1160; 1072; 836.

ACKNOWLEDGMENTS

We thank the following agencies for support: CNPq, CAPES, FAPESP and FAPERGS.

References

[1] (a) N. Petragnani: *Tellurium in Organic Synthesis*, Academic Press, Great Britain (1994). (b) J.V. Comasseto, L.W. Ling, N. Petragnani, H.A. Stefani, *Synthesis*, 373 (1997).

[2] (a) A.L. Braga, G. Zeni, L.H. Andrade, C.C. Silveira and H.A. Stefani, *Synthesis*, 39 (1998). (b) A.L. Braga, G. Zeni, L.H. Andrade and C.C. Silveira, *Synlett*, 595 (1997). (c) A.L. Braga, M.I. Marchi, L.H. Andrade and C.C. Silveira, *Synthetic Commun.*, **30**, 407 (2000).

[3] H.A. Stefani, J.V Comasseto, A. Chieffi and J. Zukerman-Schpector, *Organometallics*, **10**, 845 (1991).

[4] H.A. Stefani, D.O. Silva, N. Petragnani, L. Dornelles, J. Zukerman-Schpector and A.L. Braga, *J. Organomet. Chem.*, **562**, 127 (1998).

[5] X. Huang and Y.P. Wang, *Tetrahedron Lett.*, **37**, 7417 (1996).

[6] E.S. Lang, R.A. Burrow, A.L. Braga and L. Dornelles, *Z. Kristallogr.*, NCS **215**, 459 (2000).

[7] W.C. Still, M. Khan and A. Mitra, *J. Org. Chem*, **43**, 2923 (1978).

[8] D.D. Perrin, W.L.F. Armarego and D.R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 1966.

[9] N. Petragnani, *Tetrahedron*, **11**, 15 (1960).

[10] J.A. Cava, *J. Chem. Soc.*, 2266 (1959).