Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron 61 (2005) 7712–7718
Tetrahedron

Synthesis of ketene phenyl- and butyltelluroacetals by a Horner–Wittig route

Claudio C. Silveira,[a,*] Rodrigo Cella,[a] Antonio L. Braga,[a] Raquel G. Jacob,[a] Eder J. Lenardão[b] and Gelson Perin[b,*]

[a]*Departamento de Química, Universidade Federal de Santa Maria, UFSM, C.P. 5001, 97105-900 Santa Maria, RS, Brazil*
[b]*Departamento de Química, Universidade Federal de Pelotas, UFPel, PO Box 354, 96010-900 Pelotas, RS, Brazil*

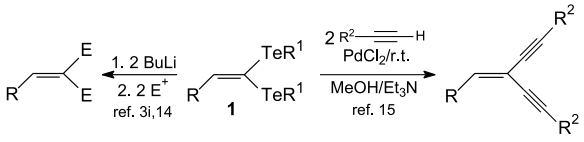
Received 31 March 2005; revised 25 May 2005; accepted 26 May 2005

Available online 17 June 2005

Abstract—New and efficient methods were developed to prepare ketene organyltelluroacetals in moderate to excellent yields. This was accomplished by reaction of phenyl- or butyltelluromethylphosphonates with phenyl- or butyltellurenyl halides and aldehydes or cyclohexanone, under basic conditions. This Horner–Wittig protocol allows the preparation of several new tri- and tetra-substituted olefins.

1. Introduction

Vinyl tellurides have recently been recognized as important synthetic reagents and intermediates, because they are used in a variety of carbon–carbon bond forming reactions.[1,2] The most useful reaction of vinyl tellurides involves transmetallation by treatment with lithium,[3] Li/Ce,[3a] Li/Zn,[4] sodium,[5] copper,[3g,6] zinc,[7] and calcium organyls[5] as well as with Grignard reagents,[3a,8] followed by the capture of the resulting vinyl anion with electrophiles. An important characteristic of this metal/metalloid exchange is that, in the majority of these reactions, the geometry of the original double bound is retained.[1] More recently, very useful applications of vinyl tellurides have emerged as powerful tools for C–C bond construction: the homocoupling[9] of vinyl tellurides and their direct cross-coupling reactions with terminal alkynes,[10] Grignard reagents,[11] alkylzinc[7a] and alkynylzinc derivatives.[7b] These are efficient protocols to prepare conjugated dienes, enynes and enediynes. The coupling can be catalyzed by palladium,[7a,b,10,11] Ni(II)[10b,11] or Co(II).[11a,d] Vinyl tellurides can also react with carbon monoxide in presence of Pd(II) salts to produce α,β-unsaturated acids, esters and butenolides.[12,13] In this way, ketene organyltelluroacetals **1**, are very useful both as vinyl 1,1-dianions[3i,14] or as vinyl 1,1-dicarbocation[15] equivalents in Te/Metal exchanges and in cross-coupling reactions, respectively (Scheme 1).



Scheme 1. High functionality of ketene organyltelluroacetals **1**.

When ketene organyltelluroacetals **1** were submitted to Pd(II)-catalyzed cross-coupling with terminal alkynes,[15] only the butyltelluroacetals afforded the respective ene-diynes in good yields. This observation is related to a previous report[3e] indicating that vinylaryltellurides gave mixtures of vinyl- and aryllithiums by transmetallation with alkyllithiums.

In spite of the high synthetic potential of ketene organyltelluroacetals, up to recent times these compounds were virtually unknown.[16]

To our knowledge, the only methods described for their preparation involve the hydrozirconation of acetylenic tellurides followed by transmetallation using a butyltellurenyl halide[16a,b] and the reaction of vinylcarbenes with diphenyl ditelluride (only two examples, in low yields).[16c] Moreover, the preparation of ketene telluroacetals with chain elongation is not possible by using these methods, which obviously limits their application in organic synthesis.

Keywords: Wittig reaction; Aldehydes; Ketene telluroacetals; Tellurium and compounds.
* Corresponding authors. Tel./fax: +55 55 220 8754 (C.C.S.); tel./fax: +55 53 275 7354 (G.P.); e-mail addresses: silveira@quimica.ufsm.br; gelson_perin@ufpel.edu.br

0040–4020/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2005.05.085

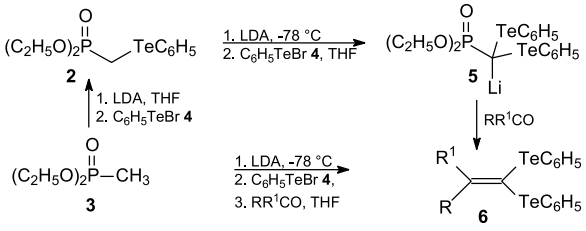
In the last years, our group has described practical and efficient methodologies for the preparation of vinyl chalcogenides based on Wittig and Horner–Wittig reactions,[17,18] including preliminary results on the synthesis of ketene phenyltelluroacetals by a Horner–Wittig methodology.[16d]

Due to our continuous interest on vinylic tellurium species, we describe here a full account on the synthesis of ketene phenyltelluroacetals and also a study of the synthesis of ketene butyltelluroacetals employing the same strategy.

2. Results and discussion

2.1. Preparation of ketene phenyltelluroacetals

Phenyltelluromethylphosphonate **2**, a reagent available on large scale and easily obtained in good yields by the reaction of diethyl methylphosphonate anion **3-Li** and phenyltellurenyl bromide **4**, was selected as starting material (Scheme 2).[19] Treatment of **2** with LDA and phenyltellurenyl bromide **4** in THF, generated the lithiated species **5** which, upon reaction with aldehydes or cyclohexanone, afforded ketene phenytelluroacetals **6a–g**, in a one-pot process (without isolation of intermediates), as depicted in Scheme 2. In most cases, good to excellent yields (72–94%) were obtained by using aromatic and aliphatic aldehydes (entries 1–5, Table 1). However, the reactions performed with acrolein and cyclohexanone gave the corresponding products in noticeably lower yields (entries 6 and 7, Table 1).

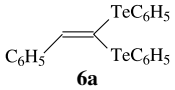
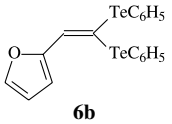
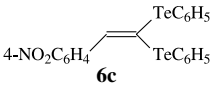
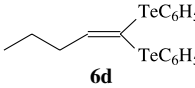
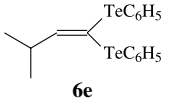
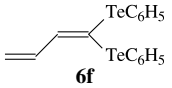
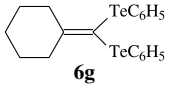


Scheme 2. Synthesis of ketene phenyltelluroacetals.

It was observed that the use of an excess of the phenyltelluromethylphosphonate **2** was required to afford **6a–g** in good yields. For example, reaction of 1.3 equiv of **2** with C_6H_5TeBr, followed by the addition of furfural, provided **6b** in 30% yield (entry 1, Table 2), while the yields increased to 64, 78 and 94% when 1.5, 1.7 and 2.0 equiv of **2**, were, respectively, employed (entries 2–4, Table 2). Therefore, and in view of the easy preparation of **2**, an excess (2 equiv) was used for the present study. Alternatively, compounds **6a–g** could be obtained directly from **3**, by reacting with LDA, phenyltellurenyl bromide **4** and then with the required carbonyl compound (Scheme 2). However, despite being an easier procedure, yield of **6b** was not satisfactory (entry 5, Table 2).

A very interesting feature was the fact that the corresponding vinyl telluride, a possible by-product resulting from the direct reaction of the anion derived from **2** with aldehydes, was not formed under the employed conditions (reactions at room temperature). It has been described that sodium salts

Table 1. Preparation of ketene bis(phenyltelluro) acetals **6** employing the strategy of Scheme 2

Entry	R	R^1	Product **6**	Reaction time (h)[a]	Yields (%)[b]
1[c]	C_6H_5	H	 **6a**	1	88
2	2-Furyl	H	 **6b**	1	94
3[d]	4-$NO_2C_6H_4$	H	 **6c**	1	72
4	$CH_3CH_2CH_2$	H	 **6d**	2	94
5	$(CH_3)_2CH$	H	 **6e**	2	84
6	CH_2CH	H	 **6f**	2	41
7	$–CH_2(CH_2)_3CH_2–$		 **6g**	2	16

[a] At room temperature.
[b] Isolated yields by column chromatography.
[c] Mp 67.9–69.2 °C (hexane).
[d] Mp 81.9–82.9 °C (hexane).

Table 2. Reaction of **2** or **3** with furfural to afford **6b**

Entry	Molar equivalents				
	2	**3**	LDA	C_6H_5TeBr	Yield (%)
1	1.3	—	2.4	1	30
2	1.5	—	2.6	1	64
3	1.7	—	2.8	1	78
4	2.0	—	3.1	1	94
5	—	1	3.1	2	45

of tellurophosphonates **2** required reflux in THF to react with aromatic aldehydes.[19] As a result of the more effective stabilizing capability of two C_6H_5Te groups the lithium intermediate **5** reacts with aromatic and aliphatic aldehydes and cyclohexanone at room temperature to give the desired products **6a–g**.

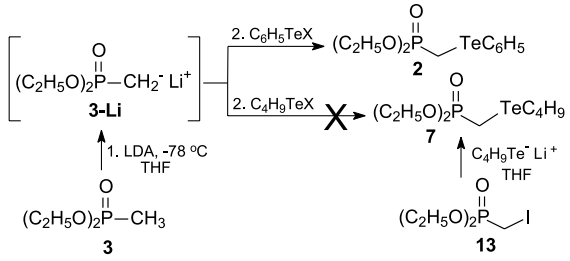
2.2. Preparation of ketene butyltelluroacetals

In view of the known cleaner Metal/Te exchange and cross-coupling reactions of vinyl butyltellurides as compared with their phenyltelluride analogs,[3e,15] we decided to perform a study on the preparation of ketene butyltelluroacetals by our Horner–Wittig route. In this way, treatment of butyltelluromethylphosphonate[19] **7** with LDA generated the lithiated species **8**, which upon reaction with butyltellurenyl iodide **9** in THF afforded the bis(butyltelluro)phosphonate intermediate **10**, as depicted in Scheme 3. The deprotonation of **10** at the expense of excess of base used, followed by the reaction with a carbonyl compound, gave the desired product **12** in a one-pot process (Scheme 3). Similar results were observed when C_4H_9TeBr [obtained in situ by the addition of Br_2 to a solution of $(C_4H_9Te)_2$ in THF] was used.

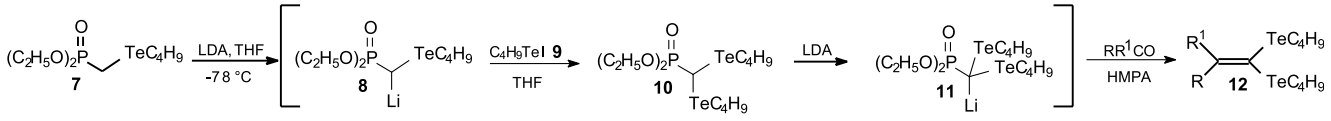
For the reactions described in Scheme 3, a detailed study of the experimental conditions was performed using benzaldehyde as the carbonyl component. By employing the optimal conditions described above for preparation of the phenyltellurium analogs **6a–g** (2 equiv of **7**, THF, rt), the yield of **12a** was unsatisfactory (entry 1, Table 3). We observed that a larger excess of the butyltellurophosphonate **7** and HMPA (1 mL) was required to afford good yields of the products **12a–h**. For example, benzaldehyde reacted with 4 equiv of **7** using THF as solvent, providing **12a** in 28% yield, while the yield increased to 72% by addition of HMPA as co-solvent (entries 2 and 3, Table 3). It was also observed that the yields were highly dependent upon the amounts of **7** and LDA (entries 4–6, Table 3), with the best results achieved by using 4 equiv of **7**, 5.1 equiv of LDA and only 1 equiv of C_4H_9TeI (entry 6, Table 3).

Although these large amounts of **7** and LDA could allow the generation of a great excess of the intermediate **8**, the formation of vinyl tellurides derived from the reaction of this species with the carbonyl compounds were not observed. Thus, 1-butyltelluro-2-phenylethene was not detected when benzaldehyde was employed, even in the presence of HMPA and under reflux. This observation reflects the greater reactivity of the phenyltelluro-phosphonate **2** when compared with its congener butyl tellurophosphonate **7**.[19]

The need of larger amounts of **7** can be explained by the lower reactivity of its anion **8-Li** towards tellurenyl halides (Scheme 3), when compared with **2-Li**. This characteristic is evidenced in the preparation of the organyltellurophosphonates **2** and **7** (Scheme 4). While phenyltellurophosphonate **2** can be prepared by the direct telluration of **3-Li** with phenyltellurenyl halides, no reaction was observed



Scheme 4. Synthesis of organyltellurophosphonates.

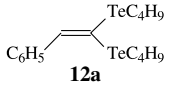
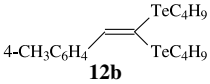
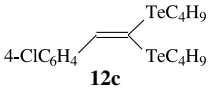
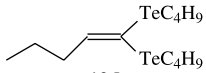
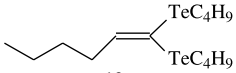
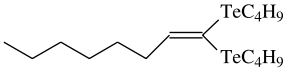
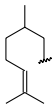
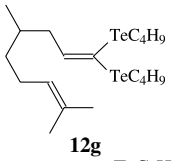
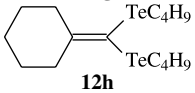


Scheme 3. Synthesis of ketene butyltelluroacetals.

Table 3. Synthesis of **12a** by reaction of **7** with benzaldehyde

Entry	Molar equivalents				
	7	LDA	C_4H_9TeI	HMPA (mL)	Yield (%)
1	2	3.1	1	—	26
2	4	6.1	2	—	28
3	4	6.1	2	1.0	72
4	2	3.1	1	1.0	29
5	3	4.1	1	1.0	54
6	4	5.1	1	1.0	75
7	3	5.1	2	1.0	53

Table 4. Preparation of ketene bis(butyltelluro) acetals **12** employing the strategy of Scheme 3

Entry	R	R^1	Product **12**	Reaction time (h)[a]	Yields (%)[b]
1	C_6H_5	H	 **12a**	2	75
2	4-MeC_6H_4	H	 **12b**	2	70
3	4-ClC_6H_4	H	 **12c**	2	63
4	$CH_3CH_2CH_2$	H	 **12d**	3	87
5	$CH_3(CH_2)_2CH_2$	H	 **12e**	3	91
6	$CH_3(CH_2)_4CH_2$	H	 **12f**	3	92
7		H	 **12g**	3	90
8	$–CH_2(CH_2)_3CH_2–$		 **12h**	3	34

[a] At room temperature.
[b] Isolated yields by column chromatography.

when butyltelluryl halides were added to **3-Li**. To circumvent this problem, an alternative procedure was envisaged to prepare **7**, based on the substitution reaction of the corresponding iodomethyl phosphonate **13** by the very nucleophilic lithium butyltellurolate in 55% yield (Scheme 4).[19]

However, the presence of the butyltellurium group in the intermediate phosphonate **8-Li** made it possible to react with butyltellurenyl halides to afford the products **12** in the presence of HMPA, via bis(butyltelluro)phosphonate **10**.

A possible explanation for the difference of reactivity between phenyltellurenyl- and butyltellurenyl halides in the alkylation step described on Scheme 4 would be the higher electrophilicity of the phenyltellurenyl group when compared to butyltellurenyl and the largest steric hindrance of the *n*-butyl group.[20]

Having in hands the best conditions for the reaction described in Scheme 3, a detailed study was performed with other carbonyl compounds with the results presented in Table 4. In most cases, good to excellent yields (63–92%) were obtained by using several aromatic and aliphatic aldehydes (Table 4). The reaction of **7** with ketones was also examined. Unfortunately, we only observed reaction with cyclohexanone and in low yield (34%, entry 8, Table 4). Other ketones such as acetophenone and 3-pentanone failed to give the desired products. Although most experiments were performed on a 1.0 mmol scale, the reactions can also be performed successfully on larger scales (e.g., 10 mmol) with comparable yields. The compounds **12a–c** (from the reaction with aromatic aldehydes) could be easily purified by column chromatography. However, the products **12d–h** were obtained as mixtures with dibutyl ditelluride, inseparable by column chromatography. In these cases, easy separations were achieved by converting the dibutyl ditelluride into dibutyl telluride, by reduction with $NaBH_4$/EtOH and subsequent reaction with *n*-butyl bromide (see Section 4).

3. Conclusions

Summarizing, we have developed a simple methodology for the synthesis of new tri- and tetra-substituted ketene bis(phenyltelluro) acetals and bis(butyltelluro) acetals. Studies involving the chemical reactivity and use of these species for the preparation of naturally occurring unsaturated compounds are currently in progress.

4. Experimental

4.1. General remarks

The ^1H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded with a 80 MHz or a 200 MHz spectrometer, as

noted. Chemical shifts are expressed as parts per million (ppm) downfield from tetramethylsilane as an internal standard. Mass spectra (EI) were obtained at 70 eV with a Hewlett Packard EM/CG HP-5988A spectrometer and elemental analyses were performed with a Vario EL Elementar Analysis System. Merck's silica gel (230–400 mesh) was used for flash chromatography. THF was distilled over sodium/benzophenone immediately before use. The aldehydes were distilled immediately before use.

4.2. General procedure for the synthesis of ketene bis(phenyltelluro) acetals 6

To a solution of LDA (3.1 mmol) in THF (4 mL) cooled to −78 °C, under nitrogen, was added dropwise a solution of **2** (0.71 g, 2 mmol) in THF (1 mL). The reaction was warmed up to 0 °C and stirred 30 min at this temperature. Then, the reaction flask was cooled to −78 °C and C_6H_5TeBr (1 mmol, prepared in situ from $C_6H_5TeTeC_6H_5$ and Br_2) in THF (2 mL) was added. At the beginning, the C_6H_5TeBr consumption was fast but at the end of the addition, a slightly red solution remained which turns yellow in ca. 20 min. The temperature was again raised to 0 °C for 30 min, the carbonyl compound (1 mmol) in THF (1 mL) was added and the reaction mixture stirred for 1–2 h at room temperature (see Table 1). The reaction was quenched by addition of water and extracted with ethyl acetate (3× 25 mL). The organic layer was dried over $MgSO_4$ and the solvent removed under vacuum. The residue was purified by column chromatography (SiO_2) using hexanes as eluent. Spectral data of **6a**–**g** are listed below.

4.2.1. 1,1-Bis(phenyltelluro)-2-phenyl-1-ethene 6a. Yield 0.454 g (88%). MS *m/z* (rel. int.) 514 (M^+-2, 9.2), 309 (10.9), 207 (49.0), 77 (100.0). ^1H NMR (80 MHz, $CDCl_3$) δ 7.00–7.50 (m, 11H); 7.60 (s, 1H); 7.65–7.93 (m, 4H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 85.8, 116.1, 118.1, 127.5, 128.1, 128.9, 129.5, 139.4, 140.6, 140.9, 145.7. Anal. Calcd for $C_{20}H_{16}Te_2$: C, 46.96; H, 3.15. Found: C, 46.83; H, 3.22.

4.2.2. 1,1-Bis(phenyltelluro)-2-(2-furyl)-1-ethene 6b. Yield 0.476 g (94%). MS *m/z* (rel. int.) 503 (M^+-3, 9.0), 205 (20.0), 77 (100.0). ^1H NMR (80 MHz, $CDCl_3$) δ 6.10 (d, J=3.4 Hz, 1H); 6.33 (dd, J=3.4 Hz, 1H); 7.10–7.33 (m, 7H); 7.42 (s, 1H); 7.62–7.75 (m, 2H); 7.80–8.00 (m, 2H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 83.0, 108.8, 111.2, 116.7, 117.7, 128.2, 128.8, 129.1, 129.4, 130.5, 139.7, 141.8, 154.9. Anal. Calcd for $C_{18}H_{14}OTe_2$: C, 43.11; H, 2.81. Found: C, 42.82; H, 3.06.

4.2.3. 1,1-Bis(phenyltelluro)-2-(4-nitrophenyl)-1-ethene 6c. Yield 0.404 g (72%). MS *m/z* (rel. int.) 557 (M^+-4, 1.9), 353 (2.6), 207 (36.0), 77 (100.0). ^1H NMR (80 MHz, $CDCl_3$) δ 7.07–7.22 (m, 2H); 7.23–7.41 (m, 6H); 7.42 (s, 1H); 7.74–7.87 (m, 4H); 7.95–8.18 (m, 2H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 93.0, 115.1, 118.1, 123.4, 128.1, 128.9, 129.2, 129.3, 129.8, 140.0, 140.6, 140.9, 146.0, 146.6. Anal. Calcd for $C_{20}H_{15}NO_2Te_2$: C, 43.16; H, 2.72. Found: C, 43.16; H, 2.81.

4.2.4. 1,1-Bis(phenyltelluro)-1-pentene 6d. Yield 0.453 g (94%). MS *m/z* (rel. int.) 479 (M^+-3, 32.0), 207 (9.0), 145 (90.0), 77 (100.0). ^1H NMR (80 MHz, $CDCl_3$) δ 0.85 (t, J=7.1 Hz, 3H); 1.20–1.60 (m, 2H); 2.20 (q, J=7.1 Hz, 2H); 6.61 (t, J=7.0 Hz, 1H); 7.00–7.30 (m, 6H); 7.55–7.90 (m, 4H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 13.6, 22.0, 41.1, 80.2, 116.5, 118.1, 127.9, 129.1, 129.3, 138.6, 153.1. Anal. Calcd for $C_{17}H_{18}Te_2$: C, 42.76; H, 3.80. Found: C, 42.75; H, 3.70.

4.2.5. 1,1-Bis(phenyltelluro)-3-methyl-1-butene 6e. Yield 0.405 g (84%). MS *m/z* (rel. int.) 479 (M^+-3, 12.0), 207 (2.0), 145 (100.0), 77 (34.0). ^1H NMR (80 MHz, $CDCl_3$) δ 0.95 (d, J=6.4 Hz, 6H); 2.30–3.00 (m, 1H); 6.44 (d, J=8.8 Hz, 1H); 7.00–7.30 (m, 6H); 7.55–7.80 (m, 4H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 21.9, 39.0, 127.9, 128.0, 129.1, 129.3, 138.4, 138.7, 160.4. Anal. Calcd for $C_{17}H_{18}Te_2$: C, 42.76; H, 3.80. Found: C, 42.81; H, 3.73.

4.2.6. 1,1-Bis(phenyltelluro)-1,3-butadiene 6f. Yield 0.191 g (41%). MS *m/z* (rel. int.) 464 (M^+-2, 3.8), 207 (21.5) 77 (100.0). ^1H NMR (80 MHz, $CDCl_3$) δ 5.07 (dd, J=15.5, 2.5 Hz, 1H); 5.11 (dd, J=10.2, 2.5 Hz, 1H); 6.34–6.79 (m, 1H); 6.96 (d, J=10.0 Hz, 1H); 7.03–7.40 (m, 6H); 7.62–7.82 (m, 4H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 116.2, 118.4, 118.6, 128.1, 128.5, 129.2, 129.6, 138.1, 139.4, 139.6, 147.6. Anal. Calcd for $C_{16}H_{14}Te_2$: C, 41.64; H, 3.06. Found: C, 41.47; H, 2.94.

4.2.7. 1,1-Bis(phenyltelluro)-2-cyclohexanyl-ethene 6g. Yield 0.081 g (16%). MS *m/z* (rel. int.) 506 (M^+-2, 13.2), 299 (9.0), 77 (100.0). ^1H NMR (80 MHz, $CDCl_3$) δ 1.35–1.55 (m, 6H); 2.50–2.75 (m, 4H); 7.00–7.30 (m, 6H); 7.61–7.49 (m, 4H). Anal. Calcd for $C_{19}H_{20}Te_2$: C, 45.32; H, 4.00. Found: C, 45.31; H, 3.99.

4.3. General procedure for the synthesis of ketene bis(butyltelluro) acetals 12

To a solution of LDA (5.1 mmol) in THF (4 mL) cooled to −78 °C, under nitrogen, was added, dropwise, a solution of **7** (1.34 g, 4 mmol) in THF (2 mL). The reaction was warmed up to 0 °C and stirred 30 min at this temperature. The reaction flask was cooled to −78 °C, and BuTeI (1 mmol, prepared in situ from $C_4H_9TeTeC_4H_9$ and I_2) in THF (2 mL) was added. At the beginning, the tellurenyl halide consumption was fast, and at the end of the addition, a slightly red solution remained, which turns yellow in ca. 20 min. The temperature was again raised to 0 °C for 30 min, the carbonyl compound (1 mmol) in HMPA (1 mL) was added and the reaction mixture stirred for 2–3 h at room temperature (see Table 4). The reaction was quenched by addition of water and extracted with ethyl acetate (3× 25 mL). The organic layer was dried over $MgSO_4$ and the solvent removed under vacuum. The residue was purified by column chromatography (SiO_2) and eluted with hexanes, yielding **12a–c** (pure materials) and **12d–h** [mixture with $(C_4H_9Te)_2$]. For the products **12d–h**, the mixture was transferred to a Erlenmeyer flask, diluted with ethyl acetate (10 mL), 95% ethanol (5 mL) and water (10 mL). Then, *n*-butylbromide (0.11 mL, 1.0 mmol) and $NaBH_4$ (0.038 g, 1 mmol) were added (to transform the dibutylditelluride into the corresponding dibutyltelluride, which is more easily removed by distillation). After this treatment, the product was extracted with ethyl acetate (3×20 mL) and washed with water, the organic phase was dried over anhydrous $MgSO_4$ and the solvent evaporated under reduced pressure.

The dibutyltelluride was distilled off from the mixture using a Kugelhohr apparatus (50 °C/0.1 mmHg) leaving the products **12d–h** as pure materials. Spectral data of **12a–h** are listed below.

4.3.1. 1,1-Bis(butyltelluro)-2-phenyl-1-ethene 12a. Yield 0.357 g (75%). MS *m/z* (rel. int.) 474 (M^+-2, 12.3), 102 (15.6), 57 (100.0). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.86 (t, $J=7.3$ Hz, 3H); 0.94 (t, $J=7.3$ Hz, 3H); 1.25–1.55 (m, 4H); 1.6–1.8 (m, 2H); 1.8–2.0 (m, 2H); 2.74 (t, $J=7.5$ Hz, 2H); 2.92 (t, $J=7.5$ Hz, 2H); 7.20–7.38 (m, 5H); 7.96 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.8, 13.4, 13.5, 15.6, 25.1, 25.2, 33.4, 33.6, 79.6, 127.4, 128.0, 128.1, 141.0, 149.7. Anal. Calcd for $C_{16}H_{24}Te_2$: C, 40.75; H, 5.13. Found: C, 41.01; H, 5.10.

4.3.2. 1,1-Bis(butyltelluro)-2-(4-methylphenyl)-1-ethene 12b. Yield 0.343 g (70%). MS *m/z* (rel. int.) 488 (M^+-2, 13.8), 115 (64.7), 57 (100.0). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.86 (t, $J=7.2$ Hz, 3H); 0.93 (t, $J=7.2$ Hz, 3H); 1.22–1.52 (m, 4H); 1.63–1.78 (m, 2H); 1.80–1.95 (m, 2H); 2.31 (s, 3H); 2.74 (t, $J=7.4$ Hz, 2H); 2.89 (t, $J=7.4$ Hz, 2H); 7.20 (d, $J=7.9$ Hz, 2H); 7.11 (d, $J=7.9$ Hz, 2H); 7.95 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.5, 13.4, 15.5, 21.1, 24.9, 25.0, 33.2, 33.5, 78.6, 127.8, 128.5, 137.0, 137.9, 149.8. Anal. Calcd $C_{17}H_{26}Te_2$: C, 42.05; H, 5.40. Found: C, 42.27; H, 5.27.

4.3.3. 1,1-Bis(butyltelluro)-2-(4-chlorophenyl)-1-ethene 12c. Yield 0.321 g (63%). MS *m/z* (rel. int.) 508 (M^+-2, 8.8), 136 (19.1), 57 (100.0). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.86 (t, $J=7.1$ Hz, 3H); 0.93 (t, $J=7.1$ Hz, 3H); 1.22–1.53 (m, 4H); 1.63–1.78 (m, 2H); 1.80–1.96 (m, 2H); 2.74 (t, $J=7.5$ Hz, 2H); 2.90 (t, $J=7.5$ Hz, 2H); 7.22–7.31 (m, 4H); 7.86 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.0, 13.3, 13.4, 15.8, 25.0, 25.1, 33.2, 33.5, 81.1, 128.1, 129.3, 133.0, 139.1, 147.7. Anal. Calcd for $C_{16}H_{23}ClTe_2$: C, 37.98; H, 4.58. Found: C, 38.78; H, 4.37.

4.3.4. 1,1-Bis(butyltelluro)-1-pentene 12d. Yield 0.385 g (87%). MS *m/z* (rel. int.) 440 (M^+-2, 8.3), 255 (9.1), 57 (100.0). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.92 (t, $J=7.3$ Hz, 9H); 1.31–1.50 (m, 6H); 1.69–1.90 (m, 4H); 2.22 (q, $J=7.1$ Hz, 2H); 2.78 (t, $J=7.4$ Hz, 4H); 6.72 (t, $J=6.9$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 11.8, 13.5, 13.6, 13.7, 22.1, 25.2, 33.4, 33.9, 41.4, 75.9, 154.3. Anal. Calcd for $C_{13}H_{26}Te_2$: C, 35.69; H, 5.99. Found: C, 35.40; H, 5.77.

4.3.5. 1,1-Bis(butyltelluro)-1-hexene 12e.[16b] Yield 0.415 g (91%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88–0.95 (m, 9H); 1.34–1.50 (m, 8H); 1.69–1.85 (m, 4H); 2.25 (q, $J=7.0$ Hz, 2H); 2.77 (2t, $J=7.3$ Hz, 4H); 6.71 (t, $J=6.9$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 11.7, 13.4, 13.6, 13.9, 22.1, 25.1, 30.9, 33.3, 33.8, 39.0, 77.6, 154.4.

4.3.6. 1,1-Bis(butyltelluro)-1-octene 12f.[16b] Yield 0.445 g (92%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.85–0.95 (m, 9H); 1.28–1.50 (m, 12H); 1.69–1.89 (m, 4H); 2.24 (q, $J=7.0$ Hz, 2H); 2.77 (t, $J=7.2$ Hz, 2H); 2.78 (t, $J=7.2$ Hz, 2H); 6.71 (t, $J=6.9$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 11.7, 13.4, 13.6, 14.0, 22.5, 25.1, 28.7, 28.8, 31.6, 33.3, 33.8, 39.3, 75.8, 154.5.

4.3.7. 1,1-Bis(butyltelluro)-4,8-dimethyl-1,7-nonadiene 12g. Yield 0.472 g (90%). MS *m/z* (rel. int.) 506 (M^+-3, $-CH_3$, 7.5), 451 (100.0), 313 (34.5), 183 (67.0), 57 (62.0). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.92 (t, $J=7.0$ Hz, 9H); 1.60 (s, 3H); 1.68 (s, 3H); 1.00–2.50 (m, 15H); 2.78 (t, $J=7.5$ Hz, 4H); 5.09 (t, $J=6.5$ Hz, 1H); 6.73 (t, $J=6.9$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 11.7, 13.5, 13.8, 17.6, 19.6, 25.2, 25.6, 32.8, 33.5, 33.9, 36.7, 46.4, 76.7, 124.6, 131.1, 153.5. Anal. Calcd $C_{19}H_{36}Te_2$: C, 43.91; H, 6.98. Found: C, 43.57; H, 6.81.

4.3.8. 1,1-Bis(butyltelluro)-2-cyclohexanyl-ethene 12h. Yield 0.159 g (34%). MS *m/z* (rel. int.) 466 (M^+-2, 34.2), 95 (90.4), 41 (100.0). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.91 (t, $J=7.0$ Hz, 6H); 1.31–1.45 (m, 4H); 1.47–153 (m, 6H); 1.65–1.83 (m, 4H); 2.62 (t, $J=7.0$ Hz, 4H); 2.75 (t, $J=7.0$ Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.5, 14.4, 25.2, 26.4, 28.6, 33.6, 41.5, 74.3, 161.1. Anal. Calcd $C_{15}H_{28}Te_2$: C, 38.86; H, 6.09. Found: C, 38.95; H, 6.15.

Acknowledgements

The authors acknowledge the financial support provided by SCT-RS, FAPERGS, CNPq and CAPES.

References and notes

1. For reviews on preparation and reactivity of vinyl tellurides, see: (a) Petragnani, N.; Stefani, H. A. *Tetrahedron* **2005**, *61*, 1613. (b) Vieira, M. L.; Zinn, F. K.; Comasseto, J. V. *J. Braz. Chem. Soc.* **2001**, *12*, 586. (c) Barrientos-Astigarraga, R. E.; Castelani, P.; Comasseto, J. V.; Formiga, H. B.; Silva, N. C.; Sumida, C. Y.; Vieira, M. L. *J. Organomet. Chem.* **2001**, *623*, 43. (d) Comasseto, J. V.; Barrientos-Astigarraga, R. E. *Aldrichim. Acta* **2000**, *33*, 66. (e) Comasseto, J. V.; Ling, L. W.; Petragnani, N.; Stefani, H. A. *Synthesis* **1997**, 373.
2. Petragnani, N. *Best Synthetic Methods—Tellurium in Organic Synthesis*; Academic: , 1994.
3. (a) Huang, Y. Z.; Mo, X. S. *Synlett* **1998**, 93. (b) Mo, X. S.; Huang, Y. Z. *Tetrahedron Lett.* **1995**, *36*, 3539. (c) Dabdoub, M. J.; Begnini, M. L.; Cassol, T. M.; Guerrero, P. G., Jr.; Silveira, C. C. *Tetrahedron Lett.* **1995**, *36*, 7623. (d) Hiiro, T.; Kambe, N.; Ogawa, A.; Miyoshi, N.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1187. (e) Barros, S. M.; Comasseto, J. V.; Berriel, J. N. *Tetrahedron Lett.* **1989**, *30*, 7353. (f) Barros, S. M.; Dabdoub, M. J.; Dabdoub, V. B.; Comasseto, J. V. *Organometallics* **1989**, *8*, 1661. (g) Ogawa, A.; Tsuboi, Y.; Obayashi, R.; Yokoyama, K.; Ryu, I.; Sonoda, N. *J. Org. Chem.* **1994**, *59*, 1600. (h) Dabdoub, M. J.; Dabdoub, V. B. *Tetrahedron* **1995**, *51*, 9839. (i) Dabdoub, M. J.; Jacob, R. G.; Ferreira, J. T. B.; Dabdoub, V. B.; Marques, F. A. *Tetrahedron Lett.* **1999**, *40*, 7159. (j) Dabdoub, M. J.; Dabdoub, V. B.; Comasseto, J. V. *Tetrahedron Lett.* **1992**, *33*, 2261. (k) Dabdoub, M. J.; Dabdoub, V. B.; Guerrero, P. G., Jr.; Silveira, C. C. *Tetrahedron* **1997**, *53*, 4199.
4. Huang, Y. Z.; Mo, X. S. *Tetrahedron Lett.* **1998**, *39*, 1945.
5. Kanda, T.; Sugiro, T.; Kambe, N.; Sonoda, N. *Phosphorus Sulfur Silicon Relat. Elem.* **1992**, *67*, 103.
6. (a) Tucci, F. C.; Chieffi, A.; Comasseto, J. V.; Marino, J. P.

J. Org. Chem. **1996**, *61*, 4975. (b) Comasseto, J. V.; Berriel, J. *Synth. Commun.* **1990**, *20*, 1681. (c) Moraes, D. N.; Barrientos-Astigarraga, R. E.; Castelani, P.; Comasseto, J. V. *Tetrahedron* **2000**, *56*, 3327. (d) Tucci, F. C.; Chieffi, A.; Comasseto, J. V. *Tetrahedron Lett.* **1992**, *33*, 5721. (e) Araujo, M. A.; Barrientos-Astigarraga, R. E.; Ellensohn, R. M.; Comasseto, J. V. *Tetrahedron Lett.* **1999**, *40*, 5115. (f) Barrientos-Astigarraga, R. E.; Moraes, D. N.; Comasseto, J. V. *Tetrahedron Lett.* **1999**, *40*, 265. (g) Marino, J. P.; Tucci, F. C.; Comasseto, J. V. *Synlett* **1993**, 761. (h) Araujo, M. A.; Comasseto, J. V. *Synlett* **1995**, 1145. (i) Huang, X.; Zhao, C. Q. *Synth. Commun.* **1997**, *27*, 237. (j) Chieffi, A.; Comasseto, J. V. *Tetrahedron Lett.* **1995**, *35*, 4063. (k) Chieffi, A.; Comasseto, J. V. *Synlett* **1995**, 671. (l) Huang, Y. Z.; Mo, X. S.; Wang, L. *Tetrahedron Lett.* **1998**, *39*, 419.

7. (a) Dabdoub, M. J.; Dabdoub, V. B.; Marino, J. P. *Tetrahedron Lett.* **2000**, *41*, 433. (b) Dabdoub, M. J.; Dabdoub, V. B.; Marino, J. P. *Tetrahedron Lett.* **2000**, *41*, 437. (c) Terao, J.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1996**, *37*, 4741.
8. Jang, W. B.; Oh, D. Y.; Lee, C. W. *Tetrahedron Lett.* **2000**, *41*, 5103.
9. Nishibayashi, Y.; Cho, C. S.; Ohe, K.; Uemura, S. *J. Organomet. Chem.* **1996**, *526*, 335.
10. (a) Zeni, G.; Comasseto, J. V. *Tetrahedron Lett.* **1999**, *40*, 4619. (b) Silveira, C. C.; Braga, A. L.; Vieira, A. S.; Zeni, G. *J. Org. Chem.* **2003**, *68*, 662.
11. (a) Uemura, S.; Fukuzawa, S.; Patil, S. R. *J. Organomet. Chem.* **1983**, *243*, 9. (b) Gerard, J.; Hevesi, L. *Tetrahedron* **2001**, *57*, 9109. (c) Huang, X.; Wang, Y. P. *Tetrahedron Lett.* **1996**, *37*, 7417. (d) Uemura, S.; Fukuzawa, S. I. *Tetrahedron Lett.* **1982**, *23*, 1181.
12. For a review on Pd(II) catalyzed homo- and cross-coupling of vinyl tellurides, see: Zeni, G.; Braga, A. L.; Stefani, H. A. *Acc. Chem. Res.* **2003**, *36*, 731.
13. (a) Uemura, S.; Ohe, K.; Kim, J. R.; Kudo, K.; Sugita, N. *J. Chem. Soc., Chem. Commun.* **1985**, 271. (b) Ohe, K.; Takahashi, H.; Uemura, S.; Sugita, N. *J. Organomet. Chem.* **1987**, *326*, 35. (c) Ohe, K.; Takahashi, H.; Uemura, S.; Sugita, N. *J. Org. Chem.* **1987**, *52*, 4859.
14. Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 410.
15. Zeni, G.; Perin, G.; Cella, R.; Jacob, R. G.; Braga, A. L.; Silveira, C. C.; Stefani, H. A. *Synlett* **2002**, *6*, 975.
16. (a) Sung, J. W.; Park, C. P.; Gil, J. M.; Oh, D. Y. *J. Chem. Soc., Perkin Trans. 1* **1997**, 591. (b) Dabdoub, M. J.; Begnini, M. L.; Guerrero, P. G., Jr. *Tetrahedron* **1998**, *54*, 2371. (c) Stang, P. J.; Roberts, K. A.; Lynch, L. E. *J. Org. Chem.* **1984**, *49*, 1653. (d) Silveira, C. C.; Perin, G.; Braga, A. L. *Tetrahedron Lett.* **1995**, *36*, 7361.
17. (a) Silveira, C. C.; Perin, G.; Braga, A. L.; Petragnani, N. *Synlett* **1995**, 58. (b) Silveira, C. C.; Perin, G.; Boeck, P.; Braga, A. L.; Petragnani, N. *J. Organomet. Chem.* **1999**, *584*, 44. (c) Silveira, C. C.; Perin, G.; Braga, A. L.; Dabdoub, M. J.; Jacob, R. G. *Tetrahedron* **1999**, *55*, 7421. (d) Silveira, C. C.; Perin, G.; Braga, A. L.; Dabdoub, M. J.; Jacob, R. G. *Tetrahedron* **2001**, *57*, 5953.
18. For a review on preparation of vinyl chalcogenides by Wittig and Horner–Wittig reactions, see: Silveira, C. C.; Perin, G.; Jacob, R. G.; Braga, A. L. *Phosphorus, Sulfur Silicon* **2001**, *172*, 55.
19. Lee, C. W.; Koh, Y. J.; Oh, D. Y. *J. Chem. Soc., Perkin Trans. 1* **1994**, 717.
20. For a discussion regarding the steric factors see: Newman, M. S. *J. Am. Chem. Soc.* **1950**, *72*, 4783.